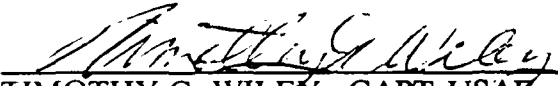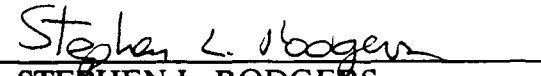## NOTICE

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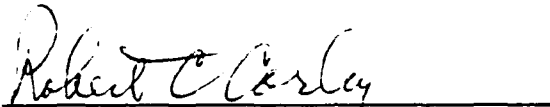
FOREWORD

This final report was submitted by Rockwell International, Rocketdyne Division on completion of contract F04611–86–C–0074 with the Astronautics Laboratory (AFSC), Edwards AFB CA. AL project managers were Capt. Walter Lauderdale, Capt. Steve Thompson, and Capt. Tim Wiley.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the DD Form 1473.

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A three year experimental program in the area of novel energetic materials was carried out. Target compounds included NF_5, ClF_5O, the NF_2^- and ClF_6^- anions, the ArF^+ cation, the AsF_6 radical, and $N(CH_3)_4^+$ salts of the halogen fluorides. It was shown that NF_5 cannot exist for steric reasons, and ClF_5O remained eluvise. The new compound $N(CH_3)_4^+ClF_4^-$ was prepared and characterized and is the first known combination of an organic ion with a chlorine fluoride counterion. The crystal structures of $N(CH_3)_4HF_2$ and $N(CH_3)_4F \cdot H_2NC(CH_3)CHCN$ were determined. The steric activity of the free valence electron pairs in BrF_6^- and IF_6^- has been studied and tentative evidence for the existence of a highly sensitive $N(CH_3)_4^+ClF_6^-$ salt is presented.

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Summary

Experimental efforts were carried out to synthesize novel, energetic, high oxidation state fluorine compounds involving unusual bonding situations such as hypervalency. One of the target compounds of this study was nitrogen pentafluoride, either in its covalent NF_5 or ionic $NF_4^+F^-$ form. While NF_4BF_4 was prepared in high yield by UV-photolysis of NF_3-F_2-BF_3 mixtures at -196°C in a sapphire reactor, NF_5 or $NF_4^+F^-$ could not be obtained under similar conditions from NF_3 and F_2. Attempts were also unsuccessful to prepare NF_5 or $NF_4^+F^-$ in different matrices at 5°K from NF_3 and either photolytically or microwave generated $\overset{\bullet}{F}$ atoms. These results suggested the possibility that the maximum coordination number of fluorine towards nitrogen might be only four, and that nitrogen pentafluoride cannot exist for steric reasons. This was conclusively proven by a ^{18}F radio tracer study involving the thermal decomposition of labeled $NF_4^+HF_2^-$ which showed that attack of HF_2^- on NF_4^+ occurs exclusively on fluorine and not on nitrogen.

A second focal point of this study was ClF_5O. This molecule should be an excellent liquid oxidizer and outperform ClF_5, the best presently known earth-storable oxidizer, by about 10 seconds. Attempts to either fluorinate ClF_3O or oxygenate ClF_5 using low-temperature photolysis or high-temperature, high-pressure techniques, KrF^+ salts, PtF_6 or O_2F_2 as oxidative fluorinators and either CsF or NiF_2 catalysis did not produce isolable amounts of ClF_5O. Numerous matrix isolation experiments in Ar, N_2, Xe and mixed matrices did not yield evidence for ClF_5O. Whereas either fluorination or oxygenation of low oxidation state molecules, such as ClF or O_2, can be easily achieved, higher oxidation state molecules undergo preferential fluorine or oxygen abstraction reactions.

A third area of interest involved the steric activity of free valence electron pairs in hypervalent molecules at the limits of their maximum coordination numbers. The IF_6^- and BrF_6^- anions were ideal test cases for such a study. It was shown by Raman spectroscopy that the free valence electron pair in IF_6^- is sterically active, but that the free pair in BrF_6^- is not. On the slower time scale of NMR spectroscopy, both anions were shown to be fluxional.

Attempts were unsuccessful to synthesize the unknown NF_2^- anion by a variety of displacement reactions. The failure to isolate NF_2^- salts is attributed to the very low acidity of HNF_2. Low-temperature matrix isolation experiments aimed at either the ArF^+ cation or $\overset{\bullet}{A}sF_6$ radical were also unsuccessful.

Another objective of this program was the synthesis of novel energetic materials by the combination of organic cations with strongly oxidizing counter anions. It was found that the

$N(CH_3)_4^+$ cation is exceptionally stable toward oxidizers and therefore an ideal candidate. However, it was found that high purity $N(CH_3)_4^+F^-$ is required as a starting material for these syntheses. Since pure $N(CH_3)_4F$ was not available, an improved synthesis for this material was developed, and the compound was characterized by x-ray powder diffraction and vibrational and NMR spectroscopy. In the course of this work, it was found that the ^{19}F NMR shifts previously reported for F^- in different solvents were badly in error, and that F^- reacts slowly with CH_3CN under formation of the HF_2^- and CH_2CN^- anions with the latter undergoing a condensation with a second CH_3CN to give β-aminocrotononitrile. During the recrystallization of $N(CH_3)_4F$ from CH_3CN, single crystals were obtained which were shown by x-ray diffraction to be a 1:1 adduct between $N(CH_3)_4F$ and the "dimer" of acetonitrile, β-aminocrotononitrile.

Metathetical reactions between $N(CH_3)_4F$ and alkali metal salts of halogen fluorides in CH_3CN were used to prepare the new salts $N(CH_3)_4^+BrF_4^-$ and $N(CH_3)_4^+ClF_4^-$. The latter is a powerful oxidizer and reacts explosively with water but, surprisingly, is not shock sensitive and is thermally stable up to $100°C$. It is the first known combination of a chlorine fluoride ion with an organic counter ion. During attempts to recrystallize $N(CH_3)_4ClF_4$ from CH_3CN solution, single crystals of $N(CH_3)_4HF_2$ were obtained and its crystal structure was determined.

From the reaction of $N(CH_3)_4F$ with ClF_5 in CH_3CN, a white solid was isolated. Unlike $N(CH_3)_4ClF_4$, this solid is extremely sensitive and could be $N(CH_3)_4ClF_6$. This would be the first example of a ClF_6^- salt, but its extreme sensitivity has so far precluded its positive identification.

Table of Contents

List of Tables

Introduction

The primary objective of this program was to demonstrate the feasibility of synthesizing hypervalent, high-oxidation state fluorides of nitrogen, oxygen, and the halogens. Typical target compounds were NF_5, ClF_5O, ClF_6^-, ArF^+, NF_2^-, AsF_6, and combinations of high oxidation state halogen fluoride anions with organic cations. In addition, special experimental techniques, such as low-temperature photolysis and glow-discharge, matrix-isolation spectroscopy and microwave discharge reactions were to be explored for the syntheses of these species. In the following section a brief discussion of some of the results will be given. In cases where a certain piece of work was completed, the results were summarized as manuscripts which are given in the Appendix and either have been or will be published in technical journals.
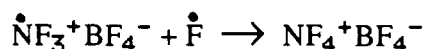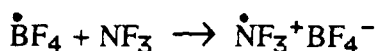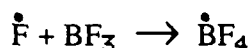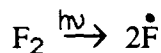
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Results and Discussion

I. Nitrogen Pentafluoride

Based on ab initio calculations (Ref. 1,2), NF_5 may be capable of existence at low temperatures either as covalent NF_5 or ionic $NF_4{}^+F^-$. A series of experiments was carried out using photolysis of NF_3 in liquid fluorine in a sapphire reactor at -196°C. The efficiency of the apparatus used and of the reaction conditions was first tested by a study of the NF_3-F_2-BF_3 system. It was shown that $NF_4{}^+BF_4{}^-$ (Ref. 3-5) was prepared in expected yields under these conditions using water filtered radiation from a focusable 1 KW high-pressure mercury arc. The NF_4BF_4 product was identified by infrared and Raman spectroscopy and showed no detectable impurities (Ref.5).

The next experiments were carried out under the same conditions as used for the synthesis of NF_4BF_4, except for using only NF_3 and F_2 as starting materials. The unreacted F_2 and NF_3 were pumped off at -186°C, leaving behind a small amount of a yellow nonvolatile residue. On warm up to ambient temperature, this residue decomposed irreversibly to gases which were noncondensible at -196°C, did not contain any NF_3 or other infrared absorbing species, and consisted of O_2 and F_2. Based on these observations, it is concluded that the small amount of product formed most likely was O_2F_2, which is known (Ref. 6) to be thermally unstable and to decompose to O_2 and F_2. The lack of observing any NF_3 in the gaseous decomposition products demonstrates that no significant amounts of NF_5 had formed under these conditions. The formation of a small amount of O_2F_2 can readily be explained by the fact that fluorine generally contains a small amount of oxygen as an impurity which forms O_2F_2 during the photolysis.

Since photolysis at -196°C did not result in the formation of detectable amounts of NF_5, we studied its possible synthesis in a N_2 matrix at 5°K. For this purpose, a matrix isolation cryostat was equipped with both quartz and CsI windows to allow UV-photolysis and the recording of infrared spectra, respectively. A supply of elemental fluorine was treated with BiF_5 at 250°C to remove any O_2 by $O_2{}^+BiF_6{}^-$ formation (Ref. 7). The infrared spectra of F_2 and of NF_3, both in N_2 matrix at a matrix ratio of 300:1 were recorded at 5°K before and after UV-photolysis. It was shown that no new infrared bands were generated by the photolysis in either sample. Photolyses were also carried out on NF_3-F_2 and BF_3-F_2 mixtures in N_2 matrices and again no new species could be detected. Since these results could have been due to either the nonexistence of the desired NF_5 or the experimental methods of generating $\overset{\bullet}{F}$ atoms by photolysis, we examined the ternary system, NF_3-F_2-BF_3 under similar conditions, i.e., photolysis of a 1:1:1 mixture in N_2 (MF=300) at 5°K. Since NF_4BF_4 is known to exist and its vibrational spectra are well known

(Ref. 3-5), but none could be observed in our matrix isolation experiments, it was concluded that the matrix isolation conditions are not conducive for NF_4BF_4 formation. This result is not surprising in view of our previously proposed reaction mechanism (Ref. 8):
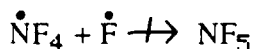
$$F_2 \xrightarrow{h\nu} 2\dot{F}$$

$$\dot{F} + BF_3 \longrightarrow \dot{B}F_4$$

$$\dot{B}F_4 + NF_3 \longrightarrow \dot{N}F_3{}^+BF_4{}^-$$

$$\dot{N}F_3{}^+BF_4{}^- + \dot{F} \longrightarrow NF_4{}^+BF_4{}^-$$

Although the $\dot{F}$ atoms should be capable of migrating through the matrix, the $\dot{B}F_4$ radical and BF_3 are too large to do so. In the case of $NF_4{}^+F^-$ or NF_5, however, this should be less of a problem because only the fluorine atoms need to migrate through the matrix:

$$NF_3 + \dot{F} \longrightarrow \dot{N}F_3{}^+F^-$$

$$\dot{N}F_3{}^+F^- + \dot{F} \longrightarrow NF_4{}^+F^-$$
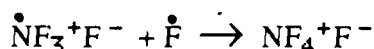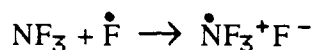
To determine if $\dot{F}$ migration is the main problem, we carried out a photolysis of neat NF_3-F_2-BF_3 at 5°K. Again, no NF_4BF_4 could be detected in the infrared spectra. This result suggested that the $\dot{F}$ atom concentrations might not have been high enough. Therefore, our equipment was modified to allow $\dot{F}$ atom generation by microwave discharge. This technique has been pioneered by Dr. Jacox at NBS and has given good results for numerous other systems (Ref. 9).

The efficiency of our experimental set up was tested by repeating an experiment previously reported by Dr. Jacox of NBS, i.e., the generation of $\dot{O}_2F$ from O_2 and $\dot{F}$ in Ar at 10°K (Ref. 10). Our results were in excellent agreement with those of Dr. Jacox.

Since $\dot{O}_2F$ was formed in good yield, we have studied the reactions of $\dot{F}$ with either NF_3 or BF_3 under the same conditions. No evidence was observed for the formation of either $\dot{N}F_4$ or NF_5 from NF_3.

$$NF_3 + \dot{F} \longrightarrow\!\!\!\!/ \ \dot{N}F_4$$

$$\dot{N}F_4 + \dot{F} \longrightarrow\!\!\!\!/ \ NF_5$$

$$\text{or } \dot{B}F_4 \text{ from } BF_3$$

$$BF_3 + \dot{F} \longrightarrow\!\!\!\!/ \ \dot{B}F_4$$
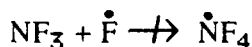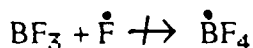
Furthermore, it was shown that NF_3 did not exhibit any significant interaction with either BF_3 or AsF_5 in an Ar matrix. Also, no evidence could be detected for the formation of $\dot{A}sF_6$ radicals from AsF_5 and microwave discharge generated $\dot{F}$ atoms. The NF_3-PtF_6 system was studied, both

in bulk in a sapphire tube and in an Ar matrix at 10°K. No evidence for any electron charge transfer from NF_3 to PtF_6 was observed.

Since up to this point all cryogenic and matrix isolation experiments aimed at NF_5 had been unsuccessful, a conclusive answer was sought whether nitrogen can coordinate to five fluorine atoms. To this end, a ^{18}F radiotracer experiment was carried out in collaboration with Prof. Schrobilgen of McMaster University. $NF_4^+HF_2^-$ which contained ^{18}F labeled HF_2^- was prepared by metathesis from NF_4SbF_6 and $CsHF_2$ in HF. It was allowed to decompose under mild conditions and the distribution of ^{18}F in the decomposition products was determined. It was found that within experimental error the NF_3 did not contain any ^{18}F. If nitrogen could coordinate five fluorine atoms, the bond polarities and charge distributions in NF_4^+ and HF_2^- would favor an attack of the F in HF_2^- on the N in NF_4^+ and hereby scrambling of the ^{18}F in the products. The observed lack of scrambling can be considered as conclusive proof for the nonexistence of pentacoordinate nitrogen and a covalent NF_5 molecule. In view of these results no further experiments aimed at covalent NF_5 were undertaken. The results from the radiotracer study were summarized in manuscript form and are given in Appendix A.

II. Chlorine Pentafluoride Oxide

Theoretical performance calculations (see Table I) indicate that ClF_5O would be an excellent earth-storable liquid oxidizer with a theoretical performance greater than any of the presently known compounds. Although the preparation of ClF_5O has previously been reported (Ref. 11), this claim has since been refuted (Ref. 12).

Table I. Specific Impulse of Liquid Propellant Candidates.

Equilibrium Expansion, Pc = 1000, ε = 35, Starred Values are Maximum

Isp's Obtained with the Rocketdyne Optimization Program

	MHF-3	B5H9	MHF-3/Al
MON -30	340.6	355.3	351.9*
ClF_3	331.7	342.3	335.4*
ClF_3O	348.9*	362.0	349.5*
ClF_3O_2	353.8*	371.3*	353.7*
ClF_5	355.0*	365.2*	355.6*
ClF_5O	364.1*	375.6*	365.4*
ClF_5/TNM	356.1*	371.4	359.0*
$ClF_5/FClO_3$	356.6*	368.7*	359.1*

The following approaches and reaction systems were studied in our attempts to prepare ClF_5O:

(i) Low temperature glow-discharge in a sapphire reactor

$$ClF_5 + O_2 \xrightarrow[-186°C]{-196°C} O_3$$

$$\xrightarrow[-126°C]{-142°C} ClF_3 + F_2$$

$$ClF_3O + F_2 \xrightarrow[-142°C]{-186°C} ClF_5 + O_3$$

$$\xrightarrow{-126°C} ClF_3 + O_2$$

$$ClF_5 + OF_2 \xrightarrow[-186°C]{-196°C} \text{NO REACTION}$$

$$\xrightarrow{-142°C} ClF_3 + F_2$$

$$FClO_3 + F_2 \xrightarrow[-142°C]{-186°C} \text{NO REACTION}$$
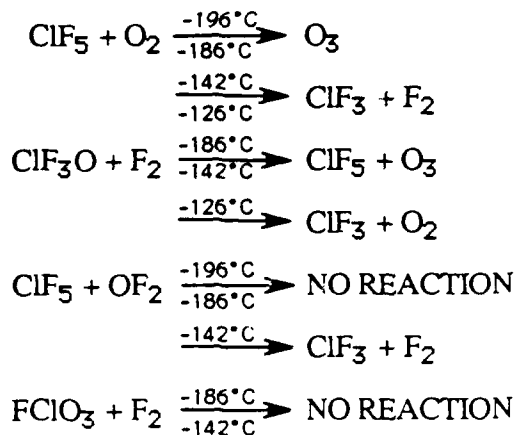
(ii) Low temperature UV-photolyses

$$ClF_3O + F_2 \xrightarrow{-186°C} ClF_5 + ClF_3 + FClO_2$$

$$\xrightarrow{-45°C} ClF_5 + FClO_3 + FClO_2$$

$$ClF_5 + OF_2 \xrightarrow[-186°C]{-196°C} \text{NO REACTION}$$

$$\xrightarrow{-142°C} ClF_3 + F_2$$

$$ClF_3 + OF_2 \xrightarrow[-186°C]{-196°C} ClF_5$$

$$Cl_2 + F_2 + O_2 \xrightarrow{-196°C} ClF_5$$

$$FClO_3 + F_2 \xrightarrow{-196°C} \text{NO REACTION}$$

$$ClF_3O + Kr + F_2 \xrightarrow{-186°C} ClF_5 + KrF_2$$
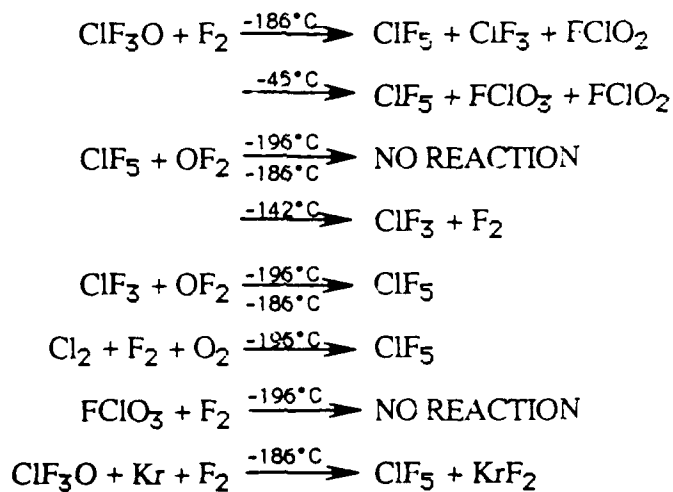
(iii) High temperature fluorination reactions

$$(ClF_2O^+)_2NiF_6{}^{2-} \xrightarrow{110°C} 2ClF_3O + NiF_2 + F_2$$

$$ClF_3O + F_2 \xrightarrow[\text{Steel, CsF cat.}]{215°C, 2000 \text{ psi}} ClF_5 \cdot ClF_3 + O_2 + FClO_2$$

$$ClF_3O + F_2 + O_2 \xrightarrow[\text{Nickel, NiF}_2 \text{ cat.}]{220°C, 3800 \text{ psi}} ClF_5 + 1/2\ O_2$$
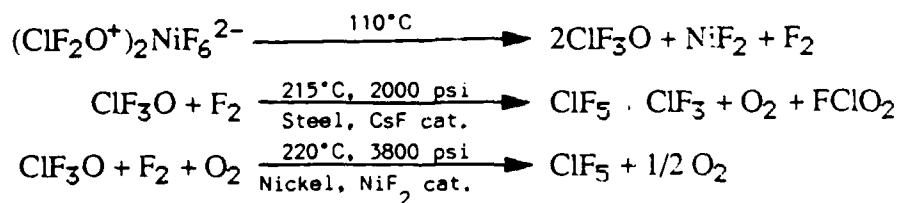
(iv) UV-photolysis in matrix at 10°K

$$ClF_3O + F_2 \xrightarrow[\text{cut off}]{420 \text{ nm}} \text{NO REACTION}$$

$$\xrightarrow[\text{cut off}]{280 \text{ nm}} ClF_3 + O_2F + O_2F_2 + OF_2$$

$$O_2 + F_2 \xrightarrow[\text{cut off}]{420 \text{ nm}} O_2F + O_2F_2$$

$$Xe + F_2 \xrightarrow[\text{cut off}]{420 \text{ nm}} XeF_2$$
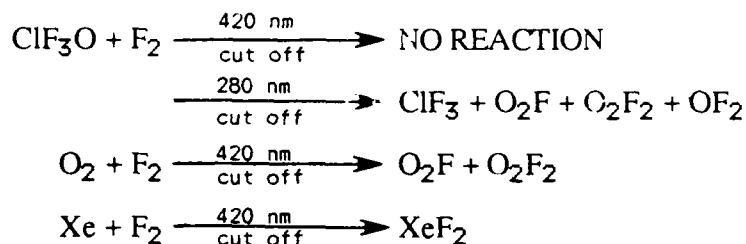
(v) Fluorination Reactions of ClF_3O with

O_2F_2:

$$ClF_3O + O_2F_2 \xrightarrow{-80°C} ClF_5 + FClO_3$$

$$Cs^+ClF_4O^- + O_2F_2 \xrightarrow{-80°C} ClF_5 + FClO_3$$

KrF_2 or KrF^+:

$$ClF_3O + KrF_2 \longrightarrow \text{NO REACTION}$$

$$Cs^+ClF_4O^- + KrF^+SbF_6^- \xrightarrow[\text{HF solution}]{\text{solids or}} CsSbF_6 + ClF_3O + KrF_2$$

NF_4^+:

$$NF_4^+HF_2^- + ClF_3O \xrightarrow{HF} ClF_2O^+HF_2^- + NF_3 + F_2$$

PtF_6:

$$ClF_3O + PtF_6 \longrightarrow ClF_2O^+PtF_6^- + 1/2\ F_2$$

FSO_2OF:

$$CsClF_4O + FOSO_2F \longrightarrow CsClF_4 + O_2 + SO_2F_2$$
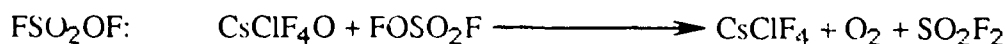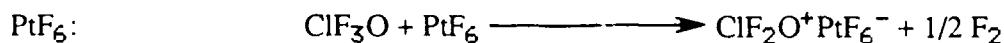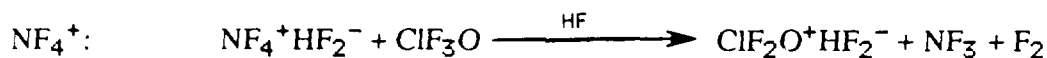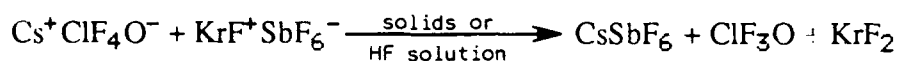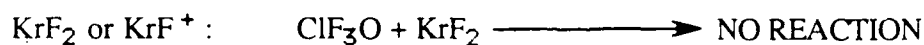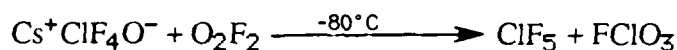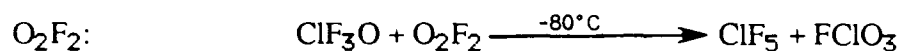
The principal approach used for the matrix isolation experiments involved the fluorination of ClF_3O with photolytically generated fluorine atoms. In this approach, the choice of appropriate filters for the photolysis is of utmost importance. The filters must be chosen in such a manner as to protect the ClF_3O starting material and an expected reaction product against photolytic decomposition while, at the same time, allowing for an efficient dissociation of the F_2 to $\overset{\bullet}{F}$ atoms.

It was found that filters which provide a cut off at wavelengths below 420 nm fully protect all the known chlorine fluorides and oxyfluorides against photolysis but still allow F_2 dissociation. This was demonstrated by showing that deposits of ClF_3O or $FClO_2$ in an Ar matrix were stable under these conditions, but that O_2 in an F_2 containing Ar matrix was efficiently converted into $\overset{\bullet}{O}_2F$ and O_2F_2.

During a visit to UC Berkeley, the late Prof. Pimentel suggested the use of xenon matrices for increased $\dot{F}$ atom yields using relatively long wavelength UV radiation. To check the usefulness of his suggestion, we carried out the photolysis of ClF_3O and F_2 in Xe with a 420 nm cut off filter. While the ClF_3O did not undergo decomposition and $\dot{F}$ atoms were efficiently generated, the only new product formed in high concentration was XeF_2. It thus appears that Xe is more readily fluorinated than ClF_3O.

Since the above results indicated that Xe matrices are not useful for the generation of new, high oxidation state chlorine compounds, such as ClF_5O, we repeated the photolysis of the ClF_3O-F_2 system in an Ar matrix using the 420 nm cut off filter. Again, the ClF_3O starting material was well protected, but no evidence was obtained for the formation of any new bands due to ClF_3O fluorination.

It thus appeared that the low-temperature fluorination of ClF_3O with photolytically generated $\dot{F}$ atoms in a matrix was not an efficient process. In order to determine whether $\dot{F}$ atom fluorinations in a matrix were feasible for this type of molecule, model reactions were carried out with either ClF or ClF_3 as a substrate. The following reactions were observed.

$$ClF + \dot{F} \rightarrow \dot{C}lF_2$$
$$O_2 + \dot{F} \rightarrow \dot{O}_2F$$
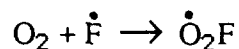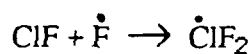
For ClF_3, however, no $\dot{F}$ addition according to

$$ClF_3 + \dot{F} \nrightarrow \dot{C}lF_4$$
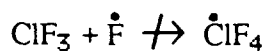
was observed. Instead, $\dot{F}$ abstraction occurred.

$$ClF_3 + \dot{F} \rightarrow \dot{C}lF_2 + F_2$$
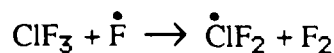
It thus appears that $\dot{F}$ atom addition proceeds well with low oxidation state molecules, but for higher oxidation states the preferred pathway is fluorine abstraction.

The use of mixed argon/nitrogen matrices was also investigated as a means of promoting the diffusion of the $\dot{F}$ atoms in the matrix, but again without apparent success. The mixed matrix concept was also applied to the reaction of AsF_5 with microwave generated $\dot{F}$ atoms, but did not provide any evidence for the $\dot{A}sF_6$ radical, an unknown species, believed to be the key intermediate in the formation of many important oxidizers, such as NF_4^+ salts (Ref. 8).

7

An alternate approach to ClF_5O was based on the replacement of one doubly bonded oxygen in ClF_3O_2 by two fluorine ligands. Although ClF_3O_2 had been synthesized by us several years ago, its synthesis had been very cumbersome making this compound virtually inaccessible for any reaction chemistry. We therefore searched for an improved synthesis of ClF_3O_2. To this end, the $FClO_2 + O_2F_2$ system was studied. The decomposition of O_2F_2 provides a ready source of $\overset{\bullet}{F}$ atoms in very high concentration at relatively low temperatures. In the case of $FClO_2$, the main reaction occurring was again an oxygen-fluorine exchange giving ClF_5 as the product, instead of an oxidative fluorination to ClF_3O_2.

In collaboration with Drs. Schrobilgen and Chirakal of McMaster University, an ^{18}F radiotracer study was carried out to determine the maximum coordination number of $Cl(+V$ and $+VII)$ towards fluorine. A displacement reaction between $ClF_6^+AsF_6^-$ and FNO was carried out and gave the following result:

$$ClF_6^+AsF_6^- + \overset{\bullet}{F}NO \longrightarrow NO^+AsF_6^- + Cl\overset{\bullet}{F}_5 + \overset{\bullet}{F}_2$$

$$77.0\% \quad 23.0\%$$
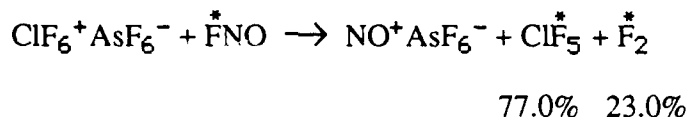
Since the observed ^{18}F activity was higher than that predicted for either one of the following two mechanisms,
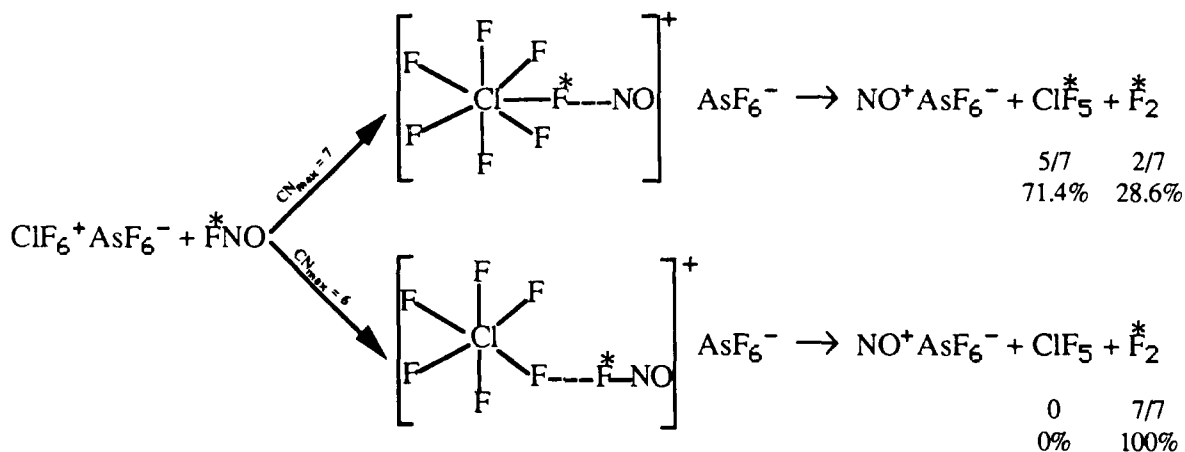
a third possibility, namely scrambling between ClF_5 and $\overset{\bullet}{F}NO$ was suspected to contribute to the above reactions

$$ClF_5 + \overset{\bullet}{F}NO \longrightarrow Cl\overset{\bullet}{F}_5 + \overset{\bullet}{F}NO$$

$$83.3\% \quad 16.7\%$$
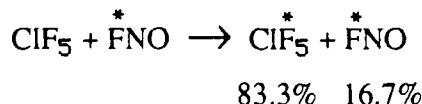
The correctness of this assumption was experimentally verified by studying the ClF_5 + $\overset{\bullet}{F}NO$ system. The observed values, i.e. $Cl\overset{\bullet}{F_5}$ (85%), $\overset{\bullet}{F}NO$ (15%), were in reasonable agreement with the predictions and suggested the existence of an unstable intermediate ClF_6^- anion. The structure of the ClF_6^- anion, i.e. the steric activity of the free valence electron pair on the chlorine central atom presented an interesting problem which will be further discussed in a subsequent section of this report and in Appendix E.

III. The ArF⁺ Cation and ȦsF₆ Radical

Since KrF^+ is the strongest presently known oxidative fluorinator (Ref. 8), ArF^+ should be an even more powerful oxidizer. Whereas ArF_2 should be thermodynamically unstable and unbound, ArF^+ should be bound and be of sufficient stability to be isolable (Ref. 13, 14). For this purpose, matrix isolation experiments between $\overset{\bullet}{F}$ atoms and Ar were carried out in the presence of AsF_5 hoping to stabilize any $\overset{\bullet}{A}rF$ radicals formed by a charge transfer to an $\overset{\bullet}{A}sF_6$ radical which based on theoretical calculation (Ref. 15) should be a powerful oxidizer with an electron affinity of 7.6 eV that is even high than that of PtF_6.

$$F_2 \rightarrow 2\overset{\bullet}{F}$$

$$\overset{\bullet}{F} + Ar \rightarrow \overset{\bullet}{A}rF$$

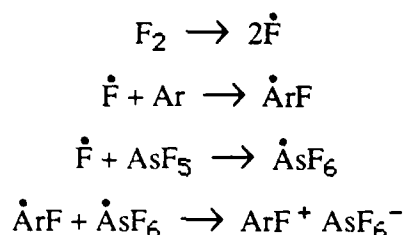$$\overset{\bullet}{F} + AsF_5 \rightarrow \overset{\bullet}{A}sF_6$$

$$\overset{\bullet}{A}rF + \overset{\bullet}{A}sF_6 \rightarrow ArF^+ AsF_6^-$$

The necessary $\overset{\bullet}{F}$ atoms were generated by a microwave discharge of F_2. Originally, a sintered alumina tube was used for the discharge, but it was found to be too porous causing the formation of by-products which rendered the observation of new species difficult. This problem was overcome by replacement of the sintered Al_2O_3 tube by a single crystal sapphire tube into which an orifice was burned with a high-power CO_2 laser. Using the sapphire discharge tube, the reaction of AsF_5 with $\overset{\bullet}{F}$ atoms in Ar was studied. However, no evidence for the formation of either $ArF^+AsF_6^-$ or the $\overset{\bullet}{A}sF_6$ radical itself was obtained.

IV. On the Synthesis of Tetramethylammonium Salts of Halogen Fluorides

A major breakthrough in oxidizer chemistry was achieved by successfully combining the ClF_4^- anion with the tetramethylammonium cation in the form of a salt which is stable up to 100°C and, most surprisingly, is not shock-sensitive. The ClF_4^- anion is an excellent incendiary for almost all hydrocarbons and many halocarbons (Ref. 16, 17). For example, tests recently carried out under

separate Air Force and Army contracts have demonstrated that $KClF_4$ is an excellent incendiary for Diesel fuel which is very difficult to ignite by conventional incendiaries.

The $[N(CH_3)_4]ClF_4$ salt was prepared in high yield and purity by the following metathetical reaction in CH_3CN at room temperature:

$$[N(CH_3)_4]F + CsClF_4 \rightarrow CsF\downarrow + [N(CH_3)_4]ClF_4$$
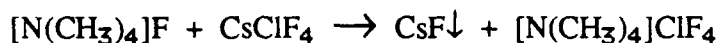
The tetramethylammonium salts of BrF_4^- and BrF_6^- were prepared and characterized in a similar manner. The results from this study were summarized in a manuscript which is given as Appendix B.

Efforts were also made to synthesize $[N(CH_3)_4]^+ClF_6^-$. Since no ClF_6^- salts are presently known, the metathetical approach used for the ClF_4^- salt could not be applied. We, therefore, used a direct reaction between $N(CH_3)_4F$ and ClF_5 in CH_3CN solution at -30°C. It was shown in a separate experiment that ClF_5 reacts only slowly with CH_3CN at this temperature and does not form a stable adduct. For the $N(CH_3)_4F + ClF_5$ reaction at -30°C, a white solid product was obtained after removal of the solvent. Based on the weight of the removed volatiles, the mass of the residue must have corresponded very closely to that expected for $[N(CH_3)_4]^+ClF_6^-$. However, the sample violently exploded before it could be weighed. The experiment was repeated and an attempt was made to record the Raman spectrum of the product at -130°C. Again, the sample detonated before a spectrum could be recorded. In view of the facts that $N(CH_3)_4ClF_4$ is stable up to 100°C and not shock sensitive and that ClF_5 does not form a stable adduct with CH_3CN at -30°C, it appears that the solid product is not $N(CH_3)_4ClF_4$ but might be the desired $N(CH_3)_4ClF_6$ salt. Further work will be required to identify this highly sensitive material.

During an attempt to grow single crystals of $N(CH_3)_4ClF_4$ from CH_3CN solution, several single crystals were obtained. An x-ray diffraction study, carried out by Prof. Bau at USC, showed them to be $[N(CH_3)_4]HF_2$. The crystal structure of $[N(CH_3)_4]HF_2$ was quite remarkable and showed an unusual packing for the HF_2^- anions. The results were summarized in manuscript form and are given as Appendix C.

A prerequisite for the above syntheses of the tetramethylammonium halogen fluoride salts was the availability of pure $N(CH_3)_4F$. It was found that pure $N(CH_3)_4F$ is not commercially available, and that most literature data on this compound were obtained for impure material. Consequently, a good synthesis was developed by neutralization of aqueous $N(CH_3)_4OH$ with HF in a N_2 atmosphere to exclude CO_2, water removal at 160°C in vacuo and recrystallization from isopropanol. Characterization of the $N(CH_3)_4F$ revealed several surprising and interesting

10

aspects. It was found that $N(CH_3)_4F$ could be purified by recrystallization from CH_3CN solution, but during an NMR study under an ongoing ARO/ONR program it was found that the F^- anion slowly reacts with CH_3CN according to:

$$2F^- + CH_3CN \rightarrow HF_2^- + CH_2CN^-$$
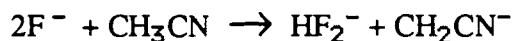
This side reaction not only generates HF_2^-, but also caused in subsequent water analyses by the Karl Fischer method the detection of significant water levels generated by the attack of the HF_2^- on the glass apparatus used for the Fischer titration:

$$4HF_2^- + SiO_2 \rightarrow SiF_6^{2-} + 2H_2O + 2F^-$$
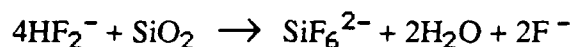
This problem was overcome by recrystallization of the $[N(CH_3)_4]F$ from isopropanol that yielded a product showing no detectable HF_2^- and a water content of less than 0.06%.

During an attempt to obtain single crystals of $N(CH_3)_4F$ by allowing hexane to slowly diffuse into a saturated CH_3CN solution of $N(CH_3)_4F$, single crystals were obtained. An x-ray structure determination by Dr. Bau's group at USC showed that the crystals were a 1:1 adduct between $N(CH_3)_4F$ and β-aminocrotononitrile. The latter is a "dimer" of acetonitrile formed by the reaction of the CH_2CN^- anion with a second CH_3CN molecule. This interesting adduct was characterized and the data, together with our data on pure $N(CH_3)_4F$, will be summarized in a future manuscript.

During a ^{19}F NMR study of $N(CH_3)_4{}^+ F^-$ in different solvents, it was found that previously published data (Ref. 18) on the chemical shift of the free F^- anion were badly in error. A brief manuscript was written to correct these data and is given as Appendix D.

V. On the Steric Activity of the Free Valence Electron Pair in IF_6^-, BrF_6^-, and ClF_6^-

In connection with our work on $[N(CH_3)_4]^+BrF_6^-$, we became interested in the structure of the BrF_6^- anion and its implications for the possible existence of ClF_6^-. The $HalF_6^-$ anions belong to the interesting class of AX_6E structures where E represents a free valence electron pair. Based on Gillespie's VSEPR rules (Ref. 19), E should be sterically active, and the AX_6 part should be non-octahedral. If, however, the maximum coordination number of A toward X equals six, then the free valence electron pair E cannot be any longer sterically active and must occupy a centro-symmetric s-orbital. Since from their reaction chemistry we know that I has a maximum coordination number of 8 toward F, while that of Br is only six, it was interesting to compare the structures of BrF_6^- and IF_6^-. It was shown that for the study of highly fluxional moieties, such as the $HalF_6^-$ anions, it is important to investigate the free ions and not the solids to eliminate the

11

influence of crystal field effects, and to use structural techniques operating on a very fast time scale, such as vibrational spectroscopy. Raman polarization measurements combined with ^{19}F NMR data for CH_3CN solutions of $Cs^+BrF_6^-$ and $Cs^+IF_6^-$ showed that on the time scale of vibrational spectroscopy BrF_6^- is octahedral and IF_6^- is distorted, while on the slower NMR time scale both anions are fluxional. Since chlorine has also a maximum coordination number of six toward fluorine, the instability of the ClF_6^- anion is attributed to the weak Lewis acidity of ClF_5 and not to steric effects. The results from this study were summarized in a manuscript which is given as Appendix E.

VI. The NF_2^- Anion

The presently known nitrogen fluorides (NF_3, NF_3O, N_2F_4, N_2F_2) are excellent oxidizers for rocket propulsion. Their main drawback is their low boiling points which render them only space-storable. If their molecular weight, however, could be increased by catenation (i.e. chain formation), one might obtain an earth-storable oxidizer with the performance of a space-storable oxidizer. A crucial starting material and key intermediate for the synthesis of such catenated nitrogen fluorides is the presently unknown NF_2^- anion. Therefore, a concerted effort was made to pursue its synthesis based on the following approach.

The $-NF_2$ group can be considered as a pseudo-halide with an effective electronegativity comparable to that of chlorine. Since HCl is a strong protic acid, HNF_2 might also be a reasonably strong acid and capable of displacing a weaker acid from its salts. A typical weak acid which is readily displaced by HCl is carbonic acid. However, the drawback of carbonic acid (and similar oxo acids) is its facile decomposition to CO_2 and H_2O. Since the NF_2^- anion is expected to be hydrolytically unstable, the use of such an oxo acid must be avoided. What is then needed is a salt of a weak, non-oxo acid which is relatively resistant towards oxidative fluorination. An ideal candidate which meets all of these requirements is HCN. It is a very weak protic acid (even weaker than carbonic acid), has no oxygen and is even resistant to fluorination by KrF_2 (Ref. 20).

To stabilize the NF_2^- anion in the form of a salt, the counterion should be as large as possible and show little tendency towards fluoride ion abstraction. The ideal cation therefore would be $N(CH_3)_4^+$ and the following reaction can be envisioned:

$$N(CH_3)_4^+CN^- + HNF_2 \longrightarrow N(CH_3)_4^+NF_2^- + HCN$$
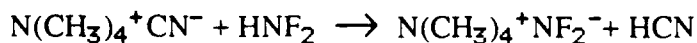
One of the problems encountered was the synthesis of pure $N(CH_3)_4^+CN^-$. After numerous futile attempts we succeeded to obtain good $N(CH_3)_4^+CN^-$ by an ion exchange between $N(CH_3)_4Br$ and an amberlite cyanide in methanol, followed by recrystallization under anhydrous conditions.

The first attempts at a displacement reaction involved the direct reaction of $N(CH_3)_4CN$ with gaseous HNF_2. However, after a short contact time of $N(CH_3)_4CN$ with about 150 torr of gaseous HNF_2, the system exploded suggesting the need for a solvent to moderate the reaction and to reduce the explosion hazards associated with HNF_2. Difluoramine and fluorine azide are probably the two most vicious detonators, and special care must be taken when working with either one of these two compounds.

We then chose to carry out the above displacement reaction between $N(CH_3)_4CN$ and HNF_2 in CH_3CN solution. However, most of the HNF_2 was recovered unchanged. Only a small amount of HCN was liberated corresponding to an equivalent amount of N_2F_2. These products are typical for an HF loss from HNF_2 according to:

$$2HNF_2 \longrightarrow N_2F_2 + 2HF$$
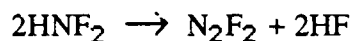
and suggests that HF was the displacing reagent. Since CH_3CN contains a basic nitrogen and can form a weak adduct with HNF_2, this adduct formation could sufficiently reduce the acidity of HNF_2 and hereby preclude the desired displacement reaction. We therefore replaced the CH_3CN by the less basic solvent $CHCl_3$. The displacement reaction was repeated but to our surprise the HNF_2 was quantitatively recovered. To test if the nonreactivity was caused by the solvent, a model reaction between KCN and HCl was carried out in $CHCl_3$. Again, no displacement occurred. This demonstrates that in an aprotic solvent, such as $CHCl_3$, the acids will not ionize and hence the displacement will not proceed.

The problem, therefore, was to find a more suitable solvent. A model reaction between KCN and HCl in anhydrous methanol was carried out and found to proceed in high yield. However, when either KCN or $N(CH_3)_4CN$ was reacted with HNF_2 in CH_3OH, most of the HNF_2 was recovered unreacted and the solid product showed no evidence for NF_2^-. An examination of the thermodynamics of the desired reactions indicated insufficient exothermicity which could result in an equilibrium lying to the side of HNF_2. Since additional calculations showed that the problem might be overcome by the use of $N(CH_3)_4CH_3O$ in place of the cyanide, the required $N(CH_3)_4CH_3O$ was synthesized and its suitability for a displacement reaction was demonstrated by reacting it with HCl. This reaction resulted in the quantitative formation of $N(CH_3)_4Cl$ according to:

$$[N(CH_3)_4]CH_3O + HCl \xrightarrow{CH_3OH} [N(CH_3)_4]Cl + CH_3OH$$
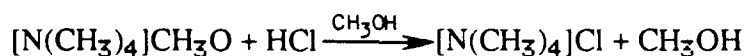
The reaction was then repeated with HNF_2 in place of HCl. The solid reaction product was treated with concentrated H_2SO_4. If the product had contained the NF_2^- anion, the H_2SO_4 treatment

should have resulted in the evolution of HNF_2. Although copious gas evolution was observed, the gas was shown to be HNCO and not HNF_2. This indicated that oxidative coupling between HNF_2 and CH_3O^- with NCO^- formation had occurred instead of the desired displacement reaction.

We have also studied aqueous solutions of HNF_2 by ^{19}F and Raman spectroscopy. The only signals detected were those of HNF_2 which persisted for several days indicating very slow hydrolysis. Pumping on these solutions allowed the recovery of most of the HNF_2.

The above series of experiments indicates that HNF_2 is a much weaker protic acid than originally assumed and explains the failures by us and others to isolate the NF_2^- anion.

Conclusions

Based on the experimental data presented in this report the following conclusions can be drawn:

1. Covalent NF_5 cannot exist for steric reasons and its synthesis should not be further pursued, while ionic $NF_4^+F^-$ might exist as an unstable compound at very low temperatures.

2. The synthesis of the NF_2^- anion by displacement reactions is foiled by the very low Broenstedt acidity of HNF_2.

3. The ClF_5O molecule remains elusive in spite of concerted efforts toward its synthesis. Oxidative fluorination of ClF_3O results in oxidation of the oxygen ligand rather than of the chlorine central atom.

4. Oxidative fluorination reactions with F atoms in inert matrices work well for low oxidation state molecules but fail for high oxidation state molecules due to competing fluorine or oxygen abstraction reactions.

5. Some experimental evidence was obtained for the possible existence of a ClF_6^- anion.

6. $[N(CH_3)_4]^+ClF_4^-$ was successfully synthesized as a thermally stable and shock insensitive compound. This is the first combination of a chlorine fluoride ion with an organic counter ion.

7. Attempts to prepare the ArF^+ cation or AsF_6 radical at low temperature in Ar matrix were unsuccessful.

8. Raman polarization data show that the free valence electron pair in BrF_6^- is sterically inactive while that in IF_6^- is active. On an NMR time scale both anions are fluxional.

9. A synthesis of pure, anhydrous $N(CH_3)_4F$ was developed, and the usefulness of the $N(CH_3)_4^+$ cation as an oxidizer resistant cation was demonstrated.

10. Acetonitrile is marginally compatible with chlorine fluorides for short time periods at subambient temperatures and offers interesting synthetic possibilities as a solvent.

11.   The free fluoride anion is surprisingly reactive and reacts with common solvents such as CH_3CN, $CHCl_3$ and CH_2Cl_2.

12.   The crystal structures of $N(CH_3)_4HF_2$ and $N(CH_3)_4F \cdot \beta$-aminocrotononitrile were determined.

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On the Existence of Pentacoordinated Nitrogen

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The thermal decomposition of NF_4HF_2 was studied by using [18F]-labeled HF_2^-. The observed distribution of [18F] among the decomposition products indicates that within experimental error the attack of HF_2^- on NF_4^+ occurs exclusively on fluorine and not on nitrogen, contrary to the predictions based on bond polarities. These results confirm the previous suggestion that the lack of pentacoordinated nitrogen species is due mainly to steric reasons.

Introduction

Hypervalency, hypercoordination, and formal expansion of the valence octet for first-row elements are and have been the subject of considerable interest and controversy.[2] Whereas hypercoordinated carbon[3] or boron[4] species are well-known, convincing experimental evidence has not been presented so far for the existence of hypercoordinated nitrogen.

It was speculated that pentacoordinated NF_5 is formed either from NF_3-F_2 by fission-fragment radiolysis at room temperature[5] or irradiation with 3-MeV bremsstrahlung[6] at -196 °C or from NF_4AsF_6 by pyrolysis at 175 °C.[7] However, all attempts have failed to confirm these speculations by either matrix-isolation experiments,[7,8] low-temperature photolysis,[9] kinetic studies[10] or isotopic exchange studies.[11]

A second pentacoordinated nitrogen species that has been studied experimentally is NH_5. On the basis of hydrogen–deuterium exchange experiments between either molten NH_4^+ salts and LiD or ND_4^+ salts and LiH, the possible intermediacy of pentacoordinated NH_4D or ND_4H was postulated.[12] However, it was subsequently shown that the observed H_2 to D_2 ratios greatly exceeded those expected for the formation of an intermediate NH_4D or ND_4H, and a catalytic isotope exchange reaction of the formed HD gas must be involved.[13]

Theoretical calculations have been carried out for NF_5,[14,15] NH_3F_2,[16] and NH_5.[12,17,18] In all cases it has been found that the pentacoordinated NX_5 species are unstable with respect to decomposition to $NX_3 + X_2$ and are less stable than the corresponding ion pairs $NX_4^+X^-$. Of the various geometries possible for a pentacoordinated NX_5 species, the trigonal-bipyramidal D_{3h} structure with two symmetrical axial bonds, i.e.
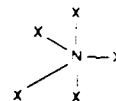
was generally found to be most favorable. Interestingly, however, it was found for NH_3F_2 that the D_{3h} geometry is only a saddle point and that the molecule is stabilized by relaxation to a C_{3v} structure that essentially is an ion pair $NH_3F^+F^-$ with only one F atom in the first coordination sphere and the second F atom at 2.00 Å from the nitrogen atom.[16] This behavior suggests that there is not enough space around nitrogen for five ligands and that steric reasons are mainly responsible for the nonexistence of a pentacoordinated nitrogen.[19]

In view of the previous failures of the experimentalists and the above conclusions by the theoreticians, the existence of a stable pentacoordinated nitrogen species is unlikely. This, however, would not preclude the possible existence of a pentacoordinate nitrogen species as a short-lived unstable intermediate, provided nitrogen could sterically accommodate five ligands. Consequently, we sought to obtain a conclusive answer to the question of whether nitrogen can sterically accommodate five ligands in its first coordination sphere.

Experimental Section

A Teflon–FEP ampule equipped with a Kel-F valve was passivated with F_2, and NF_4PF_6[9] (0.854 mmol) and dry CsF[20] (0.809 mmol) were added in the drybox. Fluorine-18 labeled HF was prepared by combining a $Ne/[^{18}F]F_2$ mixture, which was accelerator produced under conditions previously described[21] except for using a 15-MeV beam, with 1 atmosphere of H_2 at -196 °C in a 150-mL nickel can containing unlabeled anhydrous[22] HF (2.35 mmol). The H_2 and Ne were pumped off at -196 °C, and the radioactivity of the HF was measured. The labeled HF was condensed at -196 °C into the Teflon reactor, and its contents were warmed first to room temperature. While the reactor was gradually warmed to 100 °C over 1 h, the volatile products were pumped through a $^1/_4$-in. Teflon–FEP cold trap kept at -130 °C, followed by a soda lime scrubber and a second Teflon–FEP cold trap kept at -210 °C. The -130

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°C trap contained the HF and the −210 °C trap the NF$_3$, and the soda lime scrubber absorbed the F$_2$. The relative activity distribution, corrected for the elapsed time, was continuously monitored during the course of the experiment. The quantitative nature of the reaction was confirmed in a separate experiment by its material balance using unlabeled reagents under identical conditions.

Results and Discussion

A major drawback of the previously studied NH$_4$$^+$–H$^-$ system[12] is the unfavorable polarity of the N–H bonds. Since in NH$_4$$^+$ the positive charge resides on the protons and the negative one on the nitrogen, the negatively charged H$^-$ anion should attack on a proton ligand and not on the nitrogen as required for a pentacoordinated nitrogen transition state. This conclusion has been confirmed by an ab initio study, which showed that in the hydrogen abstraction reaction the pentacoordinated D_{3h} structure does not intervene either as an intermediate or a transition state. The H$^-$ ion can abstract a proton from NH$_4$$^+$ along a continuous downhill energy path.[17]

This drawback of unfavorable bond polarities can be overcome by the NF$_4$$^+$–F$^-$ system. In NF$_4$$^+$ the N–F bonds have the desired polarity for an attack of F$^-$ on nitrogen, i.e.

$$
\left[\begin{array}{c} \text{F}^{\delta^-} \\ | \\ \text{N}^{\delta^+} \\ \text{F}^{\delta^-} \text{F}^{\delta^-} \end{array} \right]^+ + \text{F}^- \longrightarrow \text{F}-\text{N}^+ \cdots \text{F}^- \qquad (1)
$$

Since NF$_4$$^+F^-$ is unknown[23] and because in the solvents known to be compatible with NF$_4$$^+$, such as HF or halogen fluorides, the F$^-$ forms complex fluoro anions, we have studied the attack of a complex fluoro anion on NF$_4$$^+$. The HF$_2$$^-$ anion appeared to be the ideal candidate because of the low thermal stability of its NF$_4$$^+$ salt[20] and its linear, highly polar structure presenting no additional steric hindrance compared to a free F$^-$ anion, i.e.
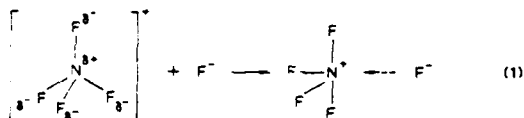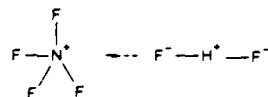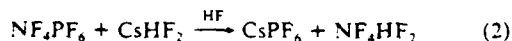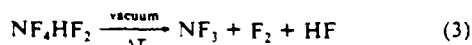
$$
\text{F}-\text{N}^+ \cdots \text{F}^- - \text{H}^+ - \text{F}^-
$$

The NF$_4$$^+HF_2$$^-$ salt can be generated from NF$_4$PF$_6$ and CsHF$_2$ in a minimal amount of anhydrous HF as a solvent.

$$
\text{NF}_4\text{PF}_6 + \text{CsHF}_2 \xrightarrow{\text{HF}} \text{CsPF}_6 + \text{NF}_4\text{HF}_2 \qquad (2)
$$

The NF$_4$HF$_2$, which is stable at room temperature in an excess of HF, decomposes on removal of HF in a dynamic vacuum between 25 and 100 °C with NF$_3$ and F$_2$ evolution.[20]

$$
\text{NF}_4\text{HF}_2 \xrightarrow[\Delta T]{\text{vacuum}} \text{NF}_3 + \text{F}_2 + \text{HF} \qquad (3)
$$

By the use of ^{18}F labeled HF$_2$$^-$ and a radioassay of the decom-

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Table I. Distribution of ^{18}F in the Reaction Products from the Pyrolysis of NF$_4$F·2.9HF

| product | [18]F activity, mCi | | |
| | found | calcd for attack on | |
		N	F
F$_2$	2.65	4.2	2.95
HF	8.2	6.1	8.55
CsPF$_6$	17.6	12.6	17.7
NF$_3$	1.2 × 10^{-3}	6.3	0
tot. activity	28.6	29.2	29.2

position products, one then can distinguish between attack of HF$_2$$^-$ on nitrogen or fluorine of NF$_4$$^+$. If there is no steric hindrance, i.e. if nitrogen can coordinate to five fluorine atoms, the HF$_2$$^-$ should attack on nitrogen because of the more favorable Coulomb forces, and hence this should result in statistical scrambling of the [18]F among NF$_3$, F$_2$, and HF. If, however, nitrogen can coordinate to only four fluorine atoms, then HF$_2$$^-$ must attack NF$_4$$^+$ at a fluorine ligand. In this case all the activity should be found in F$_2$ and HF and none in the NF$_3$. Since the PF$_6$$^-$ anion can readily exchange with the labeled HF$_2$$^-$ anion in HF solution, the CsPF$_6$ residue which is left after completion of steps 2 and 3 should also contain a statistical amount of activity.

The results of our study are summarized in Table I. As can be seen, the ^{18}F balance is excellent and the observed data are compatible only with attack of HF$_2$$^-$ on the fluorine and not the nitrogen atom of NF$_4$$^+$. The fact that a small activity reading was observed for NF$_3$ should not be interpreted as a small contribution of competing attack on nitrogen but is rather due to slight variation of the radiation background level and the associated difficulty in measuring relatively small radiation values.

In conclusion, it can be stated that within experimental error the HF$_2$$^-$ attack on NF$_4$$^+$ occurs exclusively on the fluorine atoms. Since the polarities of the bonds in both NF$_4$$^+$ and HF$_2$$^-$ would favor attack on nitrogen, the lack of attack on nitrogen is attributed to steric reasons. In view of the small size of fluorine and its ability to achieve maximum coordination numbers for most elements, the existence of pentacoordinated nitrogen species containing ligands other than fluorine must be judged even less likely, except for hydrogen, which has a smaller covalent radius than fluorine.

APPENDIX B

Tetramethylammonium Salts of ClF_4^-, BrF_4^- and BrF_6^-

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Chlorine trifluoride and its ionic ClF_2^+ and ClF_4^- salts are powerful oxidizers and generally either explode with or ignite hydrocarbons and many halocarbons.[1-4] Although BrF_3 is a less violent and vigorous fluorinating agent than ClF_3, it nevertheless reacts explosively with either water or hydrocarbons.[4] Therefore, it is not surprising that previously no salts or adducts of these compounds with organic materials have been reported. Thus, the only cations known to form ClF_4^- salts were Cs^+, Rb^+, K^+, NO^+, and NO_2^+. In the case of BrF_4^-, combinations with Na^+, Ag^+ and Ba^{2+} were also known, but again no mention of salts containing organic counterions has previously been made.[1,4]

Previous reports by Meinert had suggested that BrF_5 is less reactive than BrF_3, can be handled in CH_3CN solution,[5,6] and forms stable $[N(CH_3)_4]^+BrF_6^-$ and $[N(C_2H_5)_4]^+BrF_6^-$ salts.[7] In view of the brevity of the latter report, the lack of characterizing data for the $NR_4^+BrF_6^-$ salts, and a recent comment on the hazard of BrF_5-CH_3CN solutions,[8] it was desirable to verify Meinert's $NR_4^+BrF_6^-$ synthesis and to examine whether a similar approach could possibly be applied to the syntheses of $[N(CH_3)_4]^+$ salts of BrF_4^- and ClF_4^-.

EXPERIMENTAL SECTION

Caution: Any combination of organic materials with chlorine or bromine fluorides is potentially hazardous and should be carried out only on a small scale and with adequate safety precautions including safety shields, face masks, and protective clothing and gloves.

Materials. The CH_3CN (Baker, Bio-analyzed, having a water content of 10 ppm) was stored over P_2O_5, freshly distilled prior to its use, and handled either on a vacuum line or in the dry box. The BrF_5 (Matheson) was treated with 35 atm of F_2 at 100°C for 24 hours and then purified by fractional condensation through traps kept at -64° and -95°C, with the material retained at -95°C being used. The $CsBrF_6$,[9,10] $CsBrF_4$,[11] $CsClF_4$,[10,12] $KClF_4$,[10] and $[N(CH_3)_4]F$ [13] were prepared by literature methods.

Apparatus. Volatile halogen fluorides were handled in stainless steel vacuum lines[14] equipped with Teflon-FEP U-traps, 316-stainless steel bellows-seal valves, and a Heise Bourdon tube-type pressure gauge. The lines and other hardware were passivated with ClF_3 prior to their use. The CH_3CN was handled on a flamed out Pyrex vacuum line equipped with Teflon stopcocks. Reactions were generally carried out in Teflon-FEP ampules, closed by stainless steel valves. For the metathetical reactions, a previously described[15] apparatus was used, consisting of two Teflon-FEP U-traps interconnected through a coupling containing a porous Teflon filter. Nonvolatile materials were handled in the dry N_2 atmosphere of a glove box.

Infrared spectra were recorded in the range 4000-200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer using the 488-nm exciting line of an Ar ion laser or the 647.1-nm line of a Kr ion laser, respectively. The ^{19}F NMR spectra of CH_3CN solutions contained in heat-sealed, 5 mm o.d. Teflon-FEP tubes (Wilmad Glass Co.) were recorded at 84.6 MHz on a Varian Model EM390 spectrometer equipped with a variable temperature probe. X-ray diffraction patterns of the powdered samples in sealed 0.5 mm quartz capillaries were obtained by using a General Electric Model XRD-6 diffractometer, Ni-filtered Cu $K\alpha$ radiation, and a 114.6 mm diameter Philips camera. DSC measurements were carried out with a Perkin-Elmer Model DSC-IB using crimp-sealed aluminum pans and a heating rate of 10°/minute.

Preparation of [N(CH₃)₄]ClF₄. Inside the drybox, [N(CH$_3$)$_4$]F (1.779 mmol) and CsClF$_4$ (1.779 mmol) were placed into the bottom half of a prepassivated double U-tube metathesis apparatus[15] containing a Teflon coated magnetic stirring bar. On a flamed out glass vacuum line, dry CH$_3$CN (11 ml liquid) was condensed at -196°C into the apparatus. The mixture was allowed to warm to room temperature and was stirred for 45 minutes. The white precipitate was separated from the clear colorless solution by filtration through the Teflon filter using 2 atm of dry N$_2$ for pressurization. The CH$_3$CN was removed from the filtrate by pumping at 25°C for 15 hours, leaving behind 300 mg of [N(CH$_3$)$_4$ClF$_4$ (weight calcd for 1.779 mmol of [N(CH$_3$)$_4$]ClF$_4$ = 330 mg, corresponding to a 90.7% yield) which was identified by ^{19}F NMR, infrared and Raman spectroscopy. The white filtercake (293 mg, weight calcd for 1.779 mmol of CsF = 270 mg) consisted mainly of CsF containing about 9 mol% of [N(CH$_3$)$_4$]ClF$_4$ as an impurity.

Preparation of [N(CH₃)₄]BrF₄. The preparation of this material from [N(CH$_3$)$_4$]F and CsBrF$_4$ was carried out exactly as that described above for [N(CH$_3$)$_4$]ClF$_4$, except for using only 6 ml of CH$_3$CN as a solvent. As a result, the amount of [N(CH$_3$)$_4$]BrF$_4$ retained on the CsF filtercake increased to about 25 mol% and the yield of isolated [N(CH$_3$)$_4$]BrF$_4$ decreased to 75%.

Preparation of [N(CH₃)₄]BrF₆. The preparation of this material from [N(CH$_3$)$_4$]F and CsBrF$_6$ was carried out exactly as that described above for [N(CH$_3$)$_4$]ClF$_4$ using 13.5 ml of CH$_3$CN as a solvent. Again, the material balance was essentially quantitative, and the yield of isolated [N(CH$_3$)$_4$]BrF$_6$ was 98%.

RESULTS AND DISCUSSION

Syntheses of the [N(CH₃)₄]⁺ Salts of BrF₆⁻, BrF₄⁻ and ClF₄⁻. All three salts were prepared by metathetical reactions between [N(CH$_3$)$_4$]F and the corresponding cesium polyfluorohalate salts in dry CH$_3$CN solution at room temperature.

$$[N(CH_3)_4]F + CsHalF_n \xrightarrow{CH_3CN} CsF\downarrow + [N(CH_3)_4]HalF_n$$

23
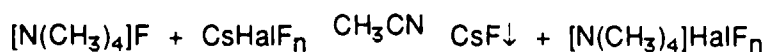
The solubility of CsF in CH_3CN is low (3.465×10^{-4} mol/l at 29.0°C) whereas those of the $[N(CH_3)_4]HalF_n$ salts and of the starting materials are much higher. For example, the solubility of $CsClF_4$ in CH_3CN at 23.5°C was found to be 4.915×10^{-2} mol/l and those of the $[N(CH_3)_4]HalF_n$ salts were typically within the range of 0.1 to 0.2 mol/l. To obtain high yields of the $[N(CH_3)_4]HalF_n$ salts in the above metathetical reactions it is, therefore, necessary to use a sufficient amount of solvent to avoid partial precipitation of the desired product.

The above metathesis based on the precipitation of CsF is similar to that previously employed by Meinert and Gross,[7]

$$[N(CH_3)_4]Cl + AgBrF_6 \xrightarrow{CH_3CN} AgCl\downarrow + [N(CH_3)_4]BrF_6$$
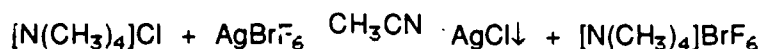
but avoids the disadvantages of using the costly and light sensitive silver salts.

For $[N(CH_3)_4]BrF_6$ we have also studied the use of direct syntheses from $[N(CH_3)_4]F$ and BrF_5 in either CH_3CN, $CFCl_3$ or an excess of liquid BrF_5 as a solvent.

$$[N(CH_3)_4]F + BrF_5 \xrightarrow{solvent} [N(CH_3)_4]BrF_6$$

In all cases the conversion of $[N(CH_3)_4]F$ to its BrF_6^- salts was incomplete requiring multiple treatments. Furthermore, $[N(CH_3)_4]BrF_4$ was always formed as a by-product, and when BrF_5 was used as the solvent, extreme care had to be taken to avoid violent reactions or explosions. Consequently, the direct synthesis is inferior to the metathesis in CH_3CN. This is not surprising since generally anions are weaker oxidizers than their parent molecules and, therefore, attack organic compounds to a lesser extent.

<u>Properties.</u> The $[N(CH_3)_4]^+$ salts of ClF_4^-, BrF_4^- and BrF_6^- are white crystallinic solids that are stable at room temperature. Their thermal stabilities were determined by DSC. The $[N(CH_3)_4]BrF_4$ salt was found to be most stable. It undergoes a highly exothermic decomposition at about 257°C and exhibits a reversible weak endotherm at 80°C that is attributed to a phase change in the solid. The $[N(CH_3)_4]BrF_6$ salt is somewhat less stable and undergoes exothermic decomposition at about 220°C. The higher stability of the BrF_4^- salt relative to its BrF_6^- analogue is also manifested by the fact that on storage of $[N(CH_3)_4]BrF_6$ at

35°C for six months most of the BrF_6^- had been reduced most likely by the cation to BrF_4^-. Therefore, $[N(CH_3)_4]BrF_6$ should not be stored over longer time periods at ambient temperature. As expected, $[N(CH_3)_4]ClF_4$ is the least stable salt in this series and undergoes a highly exothermic decomposition at about 100°C, but showed no signs of decomposition during storage at 35°C for six months.

Surprisingly, $[N(CH_3)_4]ClF_4$ was found to be insensitive to shock. A sample, when crimp-sealed in an aluminum pan and placed on a steel plate, could not be detonated by repeated hard blows with a hammer. When the flattened aluminum pan was cut open, and water was added, the sample explosively reacted with the water indicating that no decomposition had occurred prior to the contact with water.

^{19}F NMR Spectra. The relatively high solubility of $CsBrF_4$, and $CsBrF_6$, and of the $[N(CH_3)_4]^+$ salts of ClF_4^-, BrF_4^- and BrF_6^- in CH_3CN offered the possibility to study their ^{19}F NMR spectra. With the exception of BrF_4O^-,[16] essentially no NMR data have previously been reported for any chlorine or bromine fluoride anions due to the lack of compatible, non-exchanging solvents. The HF and BrF_5 solvents that are commonly used for the study of the corresponding halogen fluoride cations tend to undergo rapid exchange with the anions and, therefore, could not be used.

The ^{19}F NMR spectra of CH_3CN solutions of the ClF_4^-, BrF_4^-, and BrF_6^- salts have been recorded, and the results are summarized in Table 1. The signals of ClF_4^- and BrF_4^- were narrow singlets as expected from their known [11,12,17-19] square planar structures containing four equivalent fluorine atoms. The BrF_6^- signal was also a narrow singlet with a relatively constant line width of about 80Hz between -60° and 40°C.

A comparison of the chemical shifts of chlorine or bromine fluoride anions and cations with those of their parent molecules does not show uniform trends (see Table 2). This suggests that a simple shielding argument, i.e. that the addition of a fluoride anion to a parent molecule should add electron density and thereby result in increased shielding whereas removal of a fluoride ion should have the opposite effect, is insufficient to explain the observed data, particularly for the

25

chlorine fluorides. Obviously, a better understanding of the nature of the ^{19}F NMR shifts is required.

Since the ClF_4^-, BrF_4^- and BrF_6^- signals do not exhibit any unique fine splittings, it was necessary to record the NMR spectra of the potential impurities, i.e. F^-, HF_2^-, and HF, under the same conditions (see Table 1). Whereas our data for HF and HF_2^- are in excellent agreement with previous reports,[22,23] our value for F^- in CH_3CN solution is far outside the range of -114 to -160 ppm previously given[22] for F^- in different solvents. In particular, the shift of -150.6 ppm listed[22] for $[N(C_2H_5)_4]F$ in aqueous CH_3CN is difficult to reconcile with our results for $[N(CH_3)_4]F$. In our study, the chemical shift of F^- in dry CH_3CN was found to be -74 ppm. Upon addition of about 10% of water, two layers formed with the aqueous layer containing essentially all the fluoride ion with a chemical shift of -117 ppm. It, thus, appears that the data in reference[22] have been flawed by the presence of impurities such as HF, HF_2^- and H_2O. The correctness of our data is also supported by a plot of $\delta(^{19}F^-)$ versus $\delta(^{35}Cl^-)$ shifts for various solvents given in a recent paper by Symons.[24] Based on his plot, the chemical shifts of F^- in different solvents are strongly solvent dependant and cover a range from -73 ppm for dimethylsulfoxide to about -148 ppm for CH_3OH.

Vibrational Spectra. The infrared and Raman spectra of the solid $[N(CH_3)_4]^+$ salts of ClF_4^-, BrF_4^-, and BrF_6^- are shown in Figures 1-3, and the observed frequencies and their assignments are summarized in Table 3. The observed spectra are in excellent agreement with previous reports on the separate ions and confirm the above given ionic formulations for these salts. The assignments for the $[N(CH_3)_4]^+$ cation are based on the previous work by Heyns and DeBeer[25] and Berg[26] and do not require further comment. The bands due to the anions are denoted in the figures by their frequency values and were assigned by analogy to those of their alkali metal salts.[9,11,12,17] The fact that the observed spectra indicate no significant symmetry lowering for the anions is not surprising in view of the high symmetry of the tetramethylammonium cation.

Conclusion. The powerful oxidizer and incendiary ClF_4^- has been combined for the first time with an organic counterion. The resulting $[N(CH_3)_4]^+ClF_4^-$ salt has been isolated as a stable, nonsensitive solid. The known $[N(CH_3)_4]^+BrF_6^-$ and the new $[N(CH_3)_4]^+BrF_4^-$ salts have also been prepared and characterized.

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DIAGRAM CAPTIONS

Figure 1. Vibrational spectra of solid $[N(CH_3)_4]ClF_4$. Trace A, infrared spectrum as an AgCl

disk; traces B and C, Raman spectra at two different sensitivity levels. The bands

marked by frequency values are due to the anion.

Figure 2. Vibrational spectra of solid $[N(CH_3)_4]BrF_4$.

Figure 3. Vibrational spectra of solid $[N(CH_3)_4]BrF_6$.

Table 1. ^{19}F NMR Parameters for the ClF_4^-, BrF_4^-, and BrF_6^- Salt

Species	Chemical Shifts[a]	Solvent	Temp. (°C)	Linewidth (Hz)	Solutes
ClF_4^-	66.8	CH_3CN	-40	16	$[N(CH_3)_4]ClF_4$
BrF_4^-	-37	CH_3CN	-40	7[b]	$[N(CH_3)_4]BrF_4$, $CsBrF_4$
BrF_6^-	94	CH_3CN	-60 to 40	80	$CsBrF_6$, $[N(CH_3)_4]BrF_6$
HF	-184	CH_3CN	25	4	HF
F^-	-73.7	CH_3CN	25	2.2	$[N(CH_3)_4]F$
	-117	H_2O	25	40	$[N(CH_3)_4]F$
HF_2^-	-145.6	CH_3CN	25	3[c]	$[N(CH_3)_4]HF_2$

(a) Chemical shifts are given in ppm with negative values being upfield from the external standard $CFCl_3$. All signals were singlets except for HF_2^-.

(b) These signals exhibited significant line broadening with increasing temperature.

(c) Doublet with J_{HF} = 122 Hz.

30

Table 2. Shift Differences (ppm) from Parent Molecules for Chlorine and Bromine Fluoride Anions and Cations

Species (shift)	Shift difference from parent molecule	Reference
ANIONS		
ClF_4^- (67)	1 upfield	a
BrF_4^- (-37)	7 upfield	a
BrF_4O^- (104)	43 upfield	b
BrF_6^- (94)	72 upfield	a
CATIONS		
BrF_2O^+ (199)	52 downfield	b
BrF_4^+ (197)	31 downfield	c
ClF_2O^+ (272)	10 downfield	d
ClF_4^+ (265)	15 upfield	d
$ClF_2O_2^+$ (310)	103 upfield	d
ClF_2^+ (-23)	91 upfield	d

(a) This work. (b) Ref. 16. (c) Ref. 20. (d) Ref. 21.

31

Table 3: Vibrational Spectra of Solid [N(CH3)4]ClF4, [N(CH3)4]BrF4, and [N(CH3)4]BrF6, and Their Assignments

obsd freq. cm⁻¹ (rel intens)						assignments (point group)		
[N(CH3)4]ClF4		[N(CH3)4]BrF4		[N(CH3)4]BrF6		HalF4⁻(D4h)	BrF6⁻(D3d)	[N(CH3)4]⁺(Td)
Ra	IR	Ra	IR	Ra	IR			
	3048 m		3045 m		3048 m			$\nu_{13}(F_2)\nu as\ CH_3$
3030 (1.5)		3025 (2)		3022 (3)				$\nu_9(E)\nu as\ CH_3$
2975 sh	2975 w	2980 (0.5)	2973 vw	2970 (0.5)	2970 vw			$\nu_{14}(F_2)\nu s\ CH_3$
2948 (1)		2943 (1.5)		2945 (1.6)				$\nu_1(A_1)\nu s\ CH_3$
2905 (0+)		2908 (0+)		2905 (0+)				and combination bands
2800 (0+)		2800 (0+)		2800 (0+)				
	2581 vw		2580 vw		2583 vw			$2\nu_{17}(A_1+E+F_2)$
	2481 vw		2480 vw		2484 vw			$(\nu_{17}-\nu_7)(F_1+F_2)$
	1491 ms		1491 ms		1489 ms			$\nu_{15}(F_2)\delta as\ CH_3$
1479 (2)		1478 (3)						$\nu_6(E)\delta as\ CH_3$
1469 (3)		1462 (3)		1465 (4)				$\nu_2(A_1)\delta s\ CH_3$
1414 (1)	1418 m	1411 (1.5)	1416 m	1413 (1)	1417 m			$\nu_{16}(F_2)\delta s\ CH_3$
1290 (0.5)	1290 mw	1285 (0.5)	1288 mw	1285 (0.5)	1286 mw			$\nu_{17}(F_2)\delta rock\ CH_3$
1179 (0.5)		1179 (0 6) / 1169 (0.5)		1170 (1)				$\nu_7(E)\delta rock\ CH_3$
			1050 m					
952 (6)	953 s	948 (6)	951 s	945 (6)	949 s			$\nu_{18}(F_2)\nu as\ CN_4$
	928 w		925 w		915 w			$2\nu_{19}(A_1+E+F_2)$
780 (6)		754 (6)		750 (5)				$\nu_3(A_1)\nu s\ CN_4$
755 sh		750 sh		740 sh				$2\nu_8(A_1)$
	719 w		710 w		704 w			
553 (1)								
	550 vs,br		480 vs,br			$\nu_6(E_u)\nu as$		
508 (100)		520 (100)				$\nu_1(A_{1g})\nu s$ in phase		
				562 (59)			$\nu_1(A_{1g})\nu s$ in phase	
					490 vs,br		$\nu_4(A_{2u})$ and $\nu_6(E_u)\nu as$	
478 sh / 458 (4) / 443 (1)	465 w	472 (6)		488 (4) / 465 sh				$\nu_{19}(F_2)\delta CN_4$
				451 (100)			$\nu_5(E_g)\nu s$ out of phase	
	425 m		315 m			$\nu_2(A_{2u})\delta s$ out of plane		
415 (85)		448 (60)				$\nu_4(B_{2g})\nu s$ out of phase		
375 (1)		370 (1)						$\nu_8(E)\delta CN_4$
278 (6)		240 (10)				$\nu_3(B_{1g})\delta s$ in plane		
				239 (9)			$\nu_2(A_{1g})$ and $\nu_7(E_g)\delta s$	
				129 (1)				
				79 (2)				

32

[N(CH₃)₄]⁺ClF₄⁻

$[N(CH_3)_4]^+ClF_4^-$

425
550
508
415
278

A
B
C

FREQUENCY, CM⁻¹

TRANSMITTANCE

INTENSITY

33

$[N(CH_3)_4]^+BrF_4^-$

FREQUENCY, CM^{-1}

TRANSMITTANCE

INTENSITY

A

B

C

315

480

448

520

2,0

34

$[N(CH_3)_4]^+BrF_6^-$

APPENDIX C

Tetramethylammonium Bifluoride, Crystal Structure and Vibrational Spectra

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Dedicated to Professor Ronald J. Gillespie on the occasion of his 65th Birthday

Abstract

Single crystals of $[N(CH_3)_4]HF_2$ were obtained as a by-product during the recrystallization of $[N(CH_3)_4]ClF_4$ from CH_3CN solution. X-ray diffraction data show that $[N(CH_3)_4]HF_2$ crystallizes in the orthorhombic space group $Pmn2_1$ with Z = 2 and unit cell dimensions a = 6.611(5), b = 8.753(5), and c = 5.386(4) Å. The structure was solved by direct methods and refined by least squares to a final R = 0.055 by using 205 independent reflections. The HF_2^- anions are symmetric, exhibit an unusually short F•••F distance of 2.213(4) Å, and vibrational frequencies close to those of the free HF_2^- anion.

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Introduction

During repeated recrystallization of $[N(CH_3)_4]ClF_4$ (1) from CH_3CN, some single crystals were obtained which were identified by X-ray diffraction as $[N(CH_3)_4]HF_2$. The crystals were formed by attack of some of the $[N(CH_3)_4]ClF_4$ on the solvent. Although $[N(CH_3)_4]HF_2$ is well known (2), and crystal structures have previously been reported for the higher polybifluorides containing the $H_2F_3^-$, $H_3F_4^-$ and $H_5F_6^-$ anions (3), no structural data were available for $[N(CH_3)_4]HF_2$ itself.

The HF_2^- anion is of significant structural and theoretical interest. It is a classic example for semi-ionic three center-four electron bonding (4,5) and exhibits the strongest known hydrogen bridge bond (6) which, depending on the symmetry of the surrounding crystal field (7), can be either symmetric or asymmetric (6,8). Furthermore, strong oscillator coupling effects between the HF_2^- anions (9) occur in these salts which can result in very broad bands in the vibrational spectra and give rise to difficulties with their assignments. Thus, the assignment of the HF_2^- stretching modes has been in question until very recently (10-12). Since the tetramethylammonium cation is large, has a low positive charge over radius ratio, and is highly symmetrical, minimal ion-ion interactions are expected for $[N(CH_3)_4]^+HF_2^-$, and the HF_2^- anion should be relatively undisturbed. It was, therefore, interesting to compare the structure of the HF_2^- anion in $[N(CH_3)_4]HF_2$ with those of the free HF_2^- anion (12) and other HF_2^- salts.

Experimental

Single crystals of $[N(CH_3)_4]HF_2$ were obtained as a less soluble by-product during the recrystallization of $[N(CH_3)_4]ClF_4$ (1) from CH_3CN solution. They were separated from the $[N(CH_3)_4]ClF_4$ solution by decantation, followed by removal of last traces of solvent in a dynamic vacuum. Crystals were mounted in flamed out quartz capillaries in the dry nitrogen atmosphere of a glove box. A Nicolet/Syntex $P2_1$ automated four circle diffractometer, with Mo Kα radiation and a graphite crystal monochromator, was used for the intensity data collection. The unit cell parameters were determined by least-squares refinement of 15 centered reflections. Data were collected using the ω- scan technique for all reflections such that $4.0° <2\theta<45.0°$. Throughout the data collection, three reflections were monitored periodically, and no decay was observed. Of 206 reflections collected, 204 reflections with $I>3\sigma$ (1) were retained for the ensuing structure analysis.

The structure was solved by direct methods using the SHELXS86 system (13), of crystallographic programs. There were two space groups that are consistent with the reflection pattern: $Pmn2_1$ (#31) and $Pmmn$ (#59). The positions of the nitrogen atom and two carbon atoms of the tetramethyl ammonium cation were revealed after direct method analysis of the data for both space groups. A subsequent difference-Fourier map distinctly revealed the bifluoride anion for both space groups. However, least-squares refinement of the atomic coordinates and thermal parameters in space group $Pmmn$ (#59) resulted

in final agreement values of R = 8.34% and R_w = 13.09%, while refinement in space group Pmn2$_1$ (#31) resulted in final agreement factors of R = 5.52% and R_w = 7.47%. The ratio of agreement factors, (8.34/5.52) = 1.51, is sufficient (by Hamilton s R factor ratio test (14)) to state that space group Pmn2$_1$ (#31), with the lower R factor, is correct at the 99.5% confidence level. Details of the data collection parameters and other crystallographic information are given in Table 1, and the final atomic coordinates are summarized in Table 2.[b] The important bond lengths and angles are given in Tables 3 and 4, respectively, and Figure 1 shows a packing diagram.

The Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer using the 488-nm exciting line of an Ar ion laser or the 647.1-nm line of a Kr ion laser, respectively. Crushed single crystals in sealed Pyrex melting point capillaries were used as samples. The infrared spectrum was recorded as an AgCl disk on a Digilab Model FTS-45 spectrometer.

39

Results and Discussion

Crystal Structure. The structure of $[N(CH_3)_4]HF_2$ can be derived from a primitive cubic CsCl lattice which is orthorhombically distorted by the nonspherical HF_2^- anions. The packing in $[N(CH_3)_4]HF_2$ (see Figure 1) is identical to that recently found (15) for $[N(CH_3)_4]O_3$, except for HF_2^- being linear while O_3^- is bent. For $[N(CH_3)_4]O_3$ the alternate space group Pmmn has been suggested in which the twofold screw axis along the a axis has been eliminated. and the only symmetry element remaining along this axis is a perpendicular symmetry plane. It should be noted, however, that the bent nature of O_3^- does not necessarily require the elimination of the twofold screw axis, and that the possibility of $Pmn2_1$ should also be tested for the ozonide.

By analogy with the O_3^- salt, the large size of the $N(CH_3)_4^+$ cations minimizes the anion - anion interactions in $[N(CH_3)_4]HF_2$ and allows the HF_2^- anions to arrange in a manner (15), in which the fluorines of one HF_2^- are pointing at the fluorines of neighboring anions. In the structures of HF_2^- salts with smaller cations, such as K^+, Rb^+, or Cs^+, the negatively polarized terminal fluorine

$$\delta- \quad \delta+ \quad \delta-$$

atoms of F - H - F always point at the positively polarized hydrogen atom of a neighboring HF_2^- anion (16), as expected from Coulombic considerations. If one proceeds, however, within the family of bifluorides to salts with even smaller cations, such as Li^+ or Na^+, the HF_2^- anions are packed again in a parallel manner (16), similar to that found for the closely related linear N_3^- salts (17). It, thus, appears that for very small and very large cations, the most favorable packing conditions, i.e. a parallel arrangement of the HF_2^- anions, dominate over electrostatic dipole effects. The latter are dominant only when the cations and anions are of comparable size.

In $[N(CH_3)_4]HF_2$, all atoms, except for two methylcarbons, lie in mirror planes normal to the a axis, and the HF_2^- anions also possess a mirror plane normal to their bond line, as expected for a symmetric HF_2^- anion. Whereas the $N(CH_3)_4^+$ cation is for practical purposes an ideal tetrahedron with the expected (3, 15, 18, 19) bond lengths and angles, the F - F distance of 2.213(4) Å in HF_2^- is considerably shorter than those of 2.26-2.28 Å observed for other HF_2^- salts (16) and the free HF_2^- anion (12). This shortening is difficult to rationalize, particularly also in view of the vibrational spectrum (see below) which is very similar to that (12) of the free HF_2^- anion which has an F - F distance of 2.28 Å. It should be noted that in the alternate, but less likely (see above), Pmmn space group the HF_2^- anion exhibits a similarly short F-F distance of 2.22Å. Therefore, a change in the space group of $[N(CH_3)_4]HF_2$ from $Pmn2_1$ to Pmmn would not result in a significant change of the F - F distance.

Vibrational Spectra. The infrared and Raman spectra of ground single crystals of $[N(CH_3)_4]HF_2$ were recorded. The Raman spectrum is shown in Figure 2, and the observed frequencies together with their assignment are listed in Table 5. The bands due to the $N(CH_3)_4^+$ cation are in good agreement with

previous literature data (1) and were assigned accordingly. The infrared spectrum agreed well with a previous report (2) from which the remaining frequencies for v_3 and v_2 of the HF_2^- anion were also taken. Table 6 gives a comparison of the frequencies of the fundamental vibrations, and the F - F and F - H distances of HF_2^- in the free ion and several salts containing either symmetric or asymmetric anions. The fundamental vibrations show the expected trends. With increasing size of the cation and better isolation of the anions, the frequencies of the symmetric HF_2^- anions approach those of the free HF_2^- anion. For the asymmetric HF_2^- anions, the frequency of v_3 increases, and those of v_1 and v_2 decrease with increasing asymmetry. Therefore, the vibrational frequencies can be used for the detection of pronounced asymmetry in these anions.

The computation of standard valence force fields for HF_2^- in these salts is not rewarding in view of the uncertainties in the frequency values of v_3, caused by their large band widths, and of the very large ionic contributions to the bonding (4, 5) which are not properly reflected by these force constants. In order to account for the strong ionic contributions to the bonding in HF_2^-, ionic force fields (20) should be used which have a stretching force constant and a force constant derived from the Coulombic force. The shortening of the F - F distance of HF_2^- in its $[N(CH_3)_4]^+$ salt is not reflected by the vibrational frequencies (see Table 6). It might, therefore, be attributed to increased Coulombic forces, but other explanations, such as possibly a slight bending of the anion caused by crystal field effects or strong librations due to loose packing of the anions, cannot be ruled out.

Conclusion. The crystal structure of $[N(CH_3)_4]HF_2$ has been determined, and the vibrational spectra have been recorded. The data show that the large $[N(CH_3)_4]^+$ cations minimize the anion - anion interactions, and that the vibrational frequencies of the HF_2^- anion approach those of the free HF_2^- anion. As expected, the $[N(CH_3)_4]^+$ cations are essentially tetrahedral, and the HF_2^- anions are symmetric. The only unexpected feature which, at the present time is not fully understood and requires further investigation, is the unusually short F - F distance of 2.213(4) Å.

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Table 1. Summary of Crystal Data and Refinement Results for $[N(CH_3)_4]^+[HF_2]^-$

space group	$Pmn2_1$ (orthohombic)
a (Å)	6.611(3)
b (Å)	8.753(5)
c (Å)	5.386(4)
V ($Å^3$)	311.6(3)
molecules/unit cell	2
molecular weight (g)	113.0
crystal dimensions (mm)	0.2 x 0.25 x 1.15
calculated density (g cm^{-3})	1.203
wavelength (Å) used for data collection	0.71069
$\sin \theta / \lambda$ limit ($Å^{-1}$)	0.539
total number of reflections measured	206
number of independent reflections	205
number of reflections used in structural analysis $I > 3\sigma(I)$	204
number of variable parameters	62
final agreement factors	R(F) = 0.0552
	R(wF) = 0.0747

Table 2. Final Atomic Coordinates for [N(CH$_3$)$_4$]$^+$[HF$_2$]$^-$

Atom	x	y	z	Ueq*	pop
N 1	0.0000	0.9678(4)	0.2789	350(6)	0.5
C 2	0.1837(4)	0.8091(4)	0.2825(5)	523(6)	1.0
C 3	0.0000	1.1311(5)	0.4169(5)	441(6)	0.5
C 4	0.0000	1.1279(5)	0.1381(5)	554(6)	0.5
F 5	0.0000	0.6387(5)	0.9000(5)	899(6)	0.5
F 6	0.0000	0.6428(5)	0.6471(4)	873(6)	0.5

*$U_{eq} = (1/3)\Sigma_{ij}(U_{ij} \cdot a_i^* \cdot a_j^* \cdot a_i \cdot a_j) \times 10^4$

Table 3. Bond Distances (Å) in [N(CH$_3$)$_4$]$^+$[HF$_2$]$^-$

N 1---C 2	1.485(3)
N 1---C 3	1.494(4)
N 1---C 4	1.504(4)
F 5---F 6	2.213(4)

Table 4. Bond Angles (deg) in the [N(CH$_3$)$_4$]$^+$ cation

C2 - N1 - C2	109.7(2)
C2 - N1 - C3	108.8(2)
C2 - N1 - C4	110.3(2)
C3 - N1 - C4	109.0(2)

Table 5. Raman Spectrum of Solid $[N(CH_3)_4]^+[HF_2]^-$

obsd freq, cm^{-1} (rel intens)	assignments (point group)	
	$[N(CH_3)_4]^+$ (T_d)	HF_2^- ($D_{\infty h}$)
3036 (36)	$\nu_5(E)\nu_{as}CH_3$	
2968 (24) br	$\nu_1(A_1)\nu_sCH_3$	
1481 (71)	$\nu_6(E)\delta_{as}CH_3$	
1466 (16)	$\nu_2(A_1)\delta_sCH_3$	
1409 (7)	$\nu_{16}(F_2)\delta_sCH_3$	
1292 (5)	$\nu_{17}(F_2)\delta_{rock}CH_3$	
1193 (5)		
	$\nu_7(E)\delta_{rock}CH_3$	
1182 (6)		
956 (53)		
	$\nu_{18}(F_2)\nu_{as}CN_4$	
949 (69)		
759 (100)	$\nu_3(A_1)\nu_sCN_4$	
596 (39)		$\nu_1(\Sigma g^+)\nu_s$
458 (13)	$\nu_{19}(F_2)\delta CN_4$	
384		
(47)	$\nu_8(E)\delta NC_4$	
378		

Table 6. Comparison of the Vibrational Frequencies (cm^{-1}) and the F-F and F-H Distances of Free HF$_2^-$ with Those of Symmetric and Asymmetric HF$_2^-$ Salts

	symmetric HF$_2^-$				asymmetric HF$_2^-$	
	free Ion[a]	[N(CH$_3$)$_4$]HF$_2$	KHF$_2$[d]	NaHF$_2$[d]	BaF(HF$_2$)[e]	CH$_3$C$_6$H$_4$NH$_3$ (HF$_2$)[f]
$\nu_1(\Sigma_g^+)\nu_{sym}$	583.05	596[b]	596, 603	630	587	527
$\nu_2(\Pi_u)\delta$	1286.03	1264, 1255[c]	1233	1210, 1220	1171	1108
$\nu_3(\Sigma_u^+)\nu_{as}$	1331.15	1376[c]	≈1450	≈1500	1684	1730
r_{F-F}(Å)	2.27771(7)	2.213(4)[b]	2.277(6)	2.264(3)	2.28	2.260
r_{F-H}(Å)	1.14		1.14	1.13	1.08	1.025

(a) Reference 12

(b) This work

(c) Reference 2

(d) Reference 9

(e) Reference 8

(f) References 2 and 6

46

FREQUENCY, CM⁻¹

INTENSITY   48
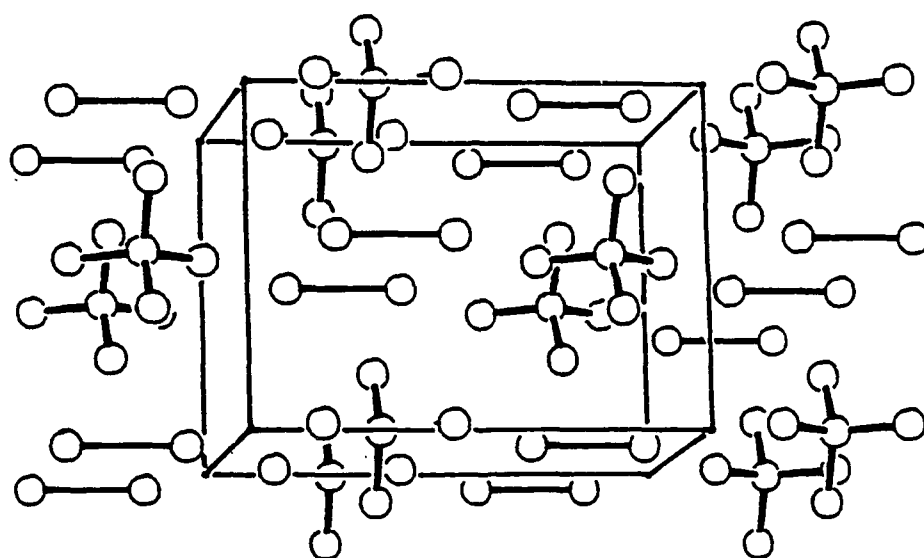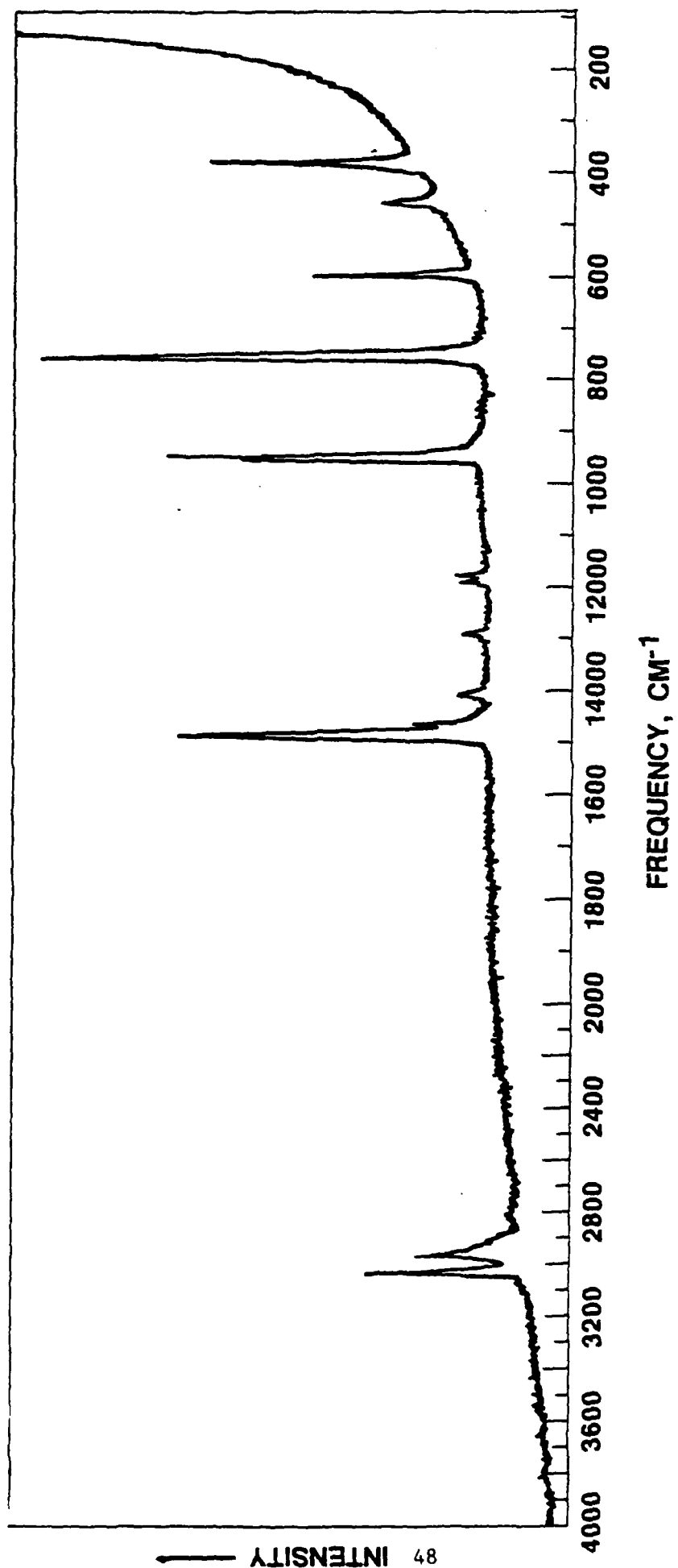
Diagram Captions

Figure 1.   Packing Diagram of $[N(CH_3)_4]^+[HF_2]^-$ viewed along the c axis.

Figure 2.   Raman Spectrum of Solid $[N(CH_3)_4]^+[HF_2]^-$.

SUPPLEMENTARY DATA

Final Temperature Factors for $[N(CH_3)_4]^+[HF_2]^-$

Atom	$U_{11}X10^4$	$U_{22}X10^4$	$U_{33}X10^4$	$U_{12}X10^4$	$U_{13}X10^4$	$U_{23}X10^4$
N 1	448(6)	263(6)	339(6)	0	0	76(6)
C 2	412(6)	427(6)	730(6)	29(6)	200(6)	-291(6)
C 3	475(6)	443(6)	407(6)	0	0	-72(6)
C 4	918(6)	393(6)	351(6)	0	0	17(6)
F 5	602(6)	1023(6)	1071(6)	0	0	-470(6)
F 6	1039(6)	926(6)	653(6)	0	0	200(6)

50

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Tetramethylammonium Bifluoride#31

H	K	L	10FO	10FC		H	K	L	10FO	10FC		H	K	L	10FO	10FC		H	K	L	10FO	10FC		H	K	L	10FO	10FC
6	0	0	99	119		5	3	1	36	37		3	0	3	19	21		5	2	4	77	74		4	1	6	28	27
2	1	0	10	11		6	3	1	17	16		5	0	3	66	66		0	3	4	28	31		5	1	6	13	14
3	1	0	20	22		0	4	1	26	25		1	1	3	91	95		1	3	4	7	7		0	2	6	21	23
7	1	0	18	24		1	4	1	36	36		2	1	3	96	98		2	3	4	49	47		1	2	6	11	12
0	2	0	126	115		2	4	1	36	36		3	1	3	66	72		3	3	4	41	39		2	2	6	52	51
2	2	0	103	96		5	4	1	11	11		4	1	3	63	58		4	3	4	19	16		3	2	6	33	30
3	2	0	199	193		0	5	1	10	10		6	1	3	51	54		5	3	4	7	11		4	3	6	30	31
7	2	0	46	44		1	5	1	43	47		0	2	3	86	81		0	4	4	86	88		0	3	6	28	28
5	2	0	44	44		2	5	1	10	11		2	2	3	39	36		1	4	4	14	17		2	3	6	15	13
0	3	0	40	35		3	5	1	50	53		3	2	3	37	37		2	4	4	79	78		2	3	6	25	23
2	3	0	16	17		2	5	1	26	23		4	2	3	75	73		3	4	4	35	34		3	3	6	23	21
2	3	0	124	110		2	0	2	64	73		6	3	3	11	9		5	4	4	46	46		4	4	6	7	5
3	3	0	49	48		3	0	2	31	32		0	3	3	24	23		0	5	4	43	46		0	4	6	13	14
4	3	0	41	41		0	0	2	48	47		2	3	3	84	78		1	5	4	9	11		1	4	6	6	6
5	3	0	14	12		1	1	2	140	147		3	3	3	109	101		3	5	4	124	125		3	4	6	6	6
0	3	0	59	56		2	1	2	118	112		4	3	3	99	98		5	5	4	39	38		0	0	7	50	51
1	4	0	34	36		3	1	2	14	16		5	3	3	121	117		0	0	5	55	55		1	1	7	6	7
2	4	0	61	63		5	1	2	55	57		0	3	3	62	60		1	1	5	151	157		3	1	7	31	31
3	4	0	65	67		6	1	2	37	32		1	4	3	19	18		2	1	5	11	10		1	1	7	88	86
4	4	0	39	39		0	2	2	49	49		3	4	3	17	17		3	1	5	46	44		2	1	7	61	58
4	4	0	30	29		1	2	2	27	25		4	4	3	25	27		4	1	5	9	8		3	1	7	53	51
5	5	0	20	19		2	2	2	49	48		4	4	3	46	44		1	2	5	34	32		4	1	7	27	25
5	5	0	15	15		3	2	2	79	81		4	4	3	20	21		2	2	5	16	15		0	2	7	26	23
5	5	0	28	29		5	2	2	79	73		5	5	3	19	19		3	2	5	36	32		1	2	7	6	8
5	0	0	111	121		0	3	2	30	28		5	5	3	20	19		1	2	5	16	15		1	2	7	11	11
7	0	0	59	50		2	3	2	38	40		5	5	3	47	47		2	2	5	33	37		3	2	7	31	31
0	0	0	12	9		3	3	2	8	9		4	0	4	132	129		2	3	5	42	41		0	3	7	33	31
3	1	—	55	47		3	3	2	8	8		7	0	4	204	199		0	3	5	16	18		3	3	7	33	30
0	1	—	160	148		0	3	2	79	77		1	1	4	59	64		1	3	5	59	63		0	3	7	20	19
4	1	—	73	72		2	3	2	51	51		0	1	4	159	153		2	3	5	30	31		0	0	8	112	111
5	1	—	86	79		3	3	2	28	29		1	1	4	6	6		4	3	5	82	81		1	1	8	59	59
2	2	—	47	43		7	3	2	42	42		2	2	4	62	59		0	4	5	21	23		2	1	8	31	33
3	2	—	23	23		0	4	2	18	19		3	2	4	66	74		2	4	5	18	17		3	1	8	12	13
0	2	—	155	145		1	4	2	33	30		4	2	4	45	44		3	4	5	42	43		4	1	8	14	16
2	2	—	37	36		2	4	2	61	60		2	3	4	22	21		0	5	5	15	13		0	2	8	12	12
3	2	—	22	25		4	4	2	17	18		3	3	4	25	25		1	6	6	121	128		2	2	8	34	34
4	3	—	61	59		5	4	2	37	39		4	3	4	70	64		2	6	6	38	37		2	2	8	20	20
6	3	—	90	86		5	5	2	16	15		0	4	4	222	210		4	6	6	38	35		3	3	9	13	16
0	3	—	9	8		2	5	2	7	6		1	4	4	92	87		0	6	6	66	68		1	0	9	8	13
2	3	—	9	9		3	5	2	19	20		2	4	4	94	89		2	6	6	25	26		2	1	9	24	24
3	4	—	9	10		3	0	3	134	141		4	4	4	39	37		3	6	6	32	36						

APPENDIX D

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF THE FLUORIDE ANION

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SUMMARY

The fluorine NMR shift of the fluoride anion in CH_3CN solution has been recorded. The observed shift of -74 ppm significantly differs from the value of -150.6 ppm recently reported. The previously observed signal is attributed to the HF_2^- anion. It is also shown that the previously reported and unexplained satellite at about -131 ppm is due to the SiF_6^{2-} anion. The chemical shifts of F^- in isopropanol, ethanol and CH_2Cl_2 have also been recorded and suggest that the F^- shifts are strongly solvent dependent.

INTRODUCTION

During a recent ^{19}F NMR study of the tetramethylammonium salts of the ClF_4^-, BrF_4^- and BrF_6^- anions in CH_3CN solution [1], we have also measured the chemical shift of the fluoride anion in this solvent. To our surprise, the observed shift dramatically deviated from the values given in a recent paper [2]. Furthermore, in that same paper a mysterious satellite had been reported for F^- which could not be explained. The purpose of this note is to explain these inconsistencies.

RESULTS AND DISCUSSION

The ^{19}F NMR chemical shifts of the F^-, HF_2^-, and SiF_6^{2-} anions were measured at 84.6 MHz on a Varian Model EM390 spectrometer using either 5 mm glass or Teflon-FEP tubes (Wilmad Glass Co.) and $CFCl_3$ as an external standard with negative shifts being upfield from the standard. The observed chemical shifts are summarized in the Table.

As can be seen from the Table, the fluoride anion in a saturated solution of $[N(CH_3)_4]F$ (prepared in our laboratory) in CH_3CN (Baker, Bioanalyzed, having an initial H_2O content of 40 ppm which was reduced to 4 ppm by distillation from P_2O_5) exhibits a chemical shift of -73 ppm. This value deviates greatly from the value of -150.6 ppm, recently reported [2]. Furthermore, it is far outside the range of -121 to -166 ppm, given in the same paper for the fluoride anion of other salts in CH_3CN. Since the previously reported values were measured for aqueous CH_3CN solutions (the water content of the CH_3CN was unfortunately not specified), we have added 10% water to our solution of $[N(CH_3)_4]F$ in CH_3CN. Two immiscible layers formed, and only the aqueous layer exhibited a ^{19}F NMR signal. Its chemical shift value (-118 ppm) is in excellent agreement with previous reports for aqueous fluoride solutions [3-6] and our own observation for an aqueous NaF solution. It appears that the large upfield shifts observed in [2] for NaF (-146.5), AgF (-166.3) and $[N(C_2H_5)_4]F$ (-150.6) are probably due to the presence of HF_2^-, HF or a combination of the two. The HF_2^- anion has a chemical shift of about -146 ppm, both in CH_3CN and aqueous solution. Whereas for the HF_2^- and F^- anions well separated signals with an H-F spin-spin coupling for HF_2^- are observed in CH_3CN solution (see the Table and [7]), a single peak with a line width of about 80Hz results for HF_2^-, F^- and HF in aqueous solution due to rapid exchange. The chemical shift of this peak depends on the mole ratios of the three species and, therefore, can vary from -118 to -170 ppm.

We have also measured the chemical shifts of F^- for solutions of $N(CH_3)_4F$ in anhydrous isopropanol ($\emptyset = -122.6$), ethanol ($\emptyset = -136.7$) and CH_2Cl_2 ($\emptyset = -97.0$). Our data show that the chemical shifts of the F^- anion are strongly solvent dependent and span a chemical shift range of at least -73 to -137 ppm. This is also supported by a previously published [8] plot of $^{19}F^-$ shifts versus those of $^{35}Cl^-$ in various solvents. Based on this plot, a chemical shift range from about -75 to -150 ppm can be deduced for the F^- anion.

Another mystery in [2] was the observation of a satellite peak at about -131 ppm in the spectra of the HF_2^- salts and those fluorides which, based on their unusually high chemical shifts, probably also were bifluorides. In our study, a similar signal was observed for all samples containing either HF_2^- or HF, but only when recorded in glass tubes and in aqueous solvents. These observations strongly suggested that this signal might be generated by attack on the glass by HF. Therefore, the most likely candidate for this signal was the SiF_6^{2-} anion. The identity of the -131 ppm signal as SiF_6^{2-} was confirmed by comparison with the spectrum

of Na_2SiF_6 in H_2O (see the Table) and the observation of ^{29}Si satellite peaks with a coupling constant $J^{29}Si\text{-}F = 110Hz$, which are characteristic for SiF_6^{2-} [9].

In conclusion, the chemical shifts previously reported in [2] for the F^- anion have been flawed by the presence of HF_2^-, HF or both in some of the samples. Furthermore, our measurements show that the chemical shift range of F^- extends over a much wider range than previously reported [2], and that the unexplained satellite at about -131 ppm is due to SiF_6^{2-}.

ACKNOWLEDGMENT

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Table. ^{19}F NMR Data for HF and $[N(CH_3)_4]^+$ or Na^+ Salts of F^-, HF_2^- and SiF_6^{2-} in either dry CH_3CN, $(CH_3)_2CHOH$, CH_3CH_2OH, CH_2Cl_2 or H_2O at Ambient Temperature

Solute	Solvent	Chemical Shift (ppm)*	Multiplicity of Peak and line width (ppm) at half height	Coupling Constant (Hz)
$[N(CH_3)_4]F$	CH_3CN	-73.2	singlet (2)	–
	$(CH_3)_2CHOH$	-122.4	singlet (4)	–
	CH_3CH_2OH	-136.7	singlet (4)	–
	CH_2Cl_2	-97.0	singlet (2)	–
$[N(CH_3)_4]HF_2$	CH_3CN	-145.6	doublet (3)	$J_{HF} = 122$
HF	CH_3CN	-184	singlet (4)	–
NaF	H_2O	-119.2	singlet (30)	–
$NaHF_2$	H_2O	-146.0	singlet (80)	–
$NaF/NaHF_2$	H_2O	-119 to -146**	singlet (80)	–
HF	H_2O	-160 to -170***	singlet	–
Na_2SiF_6	H_2O	-130	singlet (5) with ^{29}Si satellites	$J_{^{29}SiF} = 110$

* All chemical shifts are relative to the external standard $CFCl_3$ with negative values being upfield from the standard.

** Shifts depend on the mole ratio of NaF to $NaHF_2$.

*** Data from ref. 2; shifts depend on the concentration of the HF.

APPENDIX E

Steric Activity of the Central Atom Free Valence Electron Pairs in Free BrF_6^- and IF_6^- Ions

The BrF_6^- and IF_6^- anions belong to the interesting AX_6E class of compounds which contain six X ligands and one free valence electron pair E. The valence-shell electron-pair repulsion (VSEPR) Rules[1,2] predict for these compounds a distorted octahedral structure in which E becomes sterically active. While distorted structures have indeed been found for gaseous XeF_6, solid IF_6^- and $BiBr_6^{3-}$ salts, and solutions of $SbCl_6^{3-}$, $SbBr_6^{3-}$, and SbI_6^{3-}, the SeX_6^{2-} and TeX_6^{2-} ions normally have regular octahedral structures.[2] Recent work[3] on TeX_6^{2-} and SeX_6^{2-} ions has shown, however, that these ions may undergo distortion under the influence of a nonsymmetric crystal field. It thus appears that these AX_6E compounds possess rather low energy barriers toward distortion and thereby exhibit varying degrees of fluxionality. Depending on the steric and bonding conditions and the symmetry of the environment, one might, therefore, expect for these AX_6E compounds a gamut of geometries ranging from relatively rigid distorted species through highly fluxional structures to relatively rigid octahedra. The purpose of this study was to investigate the influence of steric conditions, such as the maximum coordination numbers (CN), on the structure of such AX_6E species. It was, therefore, desirable to study ions or molecules which are closely related, but differ in the maximum coordination numbers of their central atoms.

From the known reaction chemistry of iodine and bromine fluorides, one can conclude that the maximum CN of iodine towards fluorine is eight, whereas that of bromine is only six. Thus, displacement reactions of the type

$$HalF_6^+Y^- + FNO \longrightarrow HalF_7 + NO^+Y^-$$

provide IF_7 from the IF_6^+ cation, but BrF_5 and F_2 from BrF_6^+.[4] Furthermore, CsF or FNO form with IF_7 1:1 adducts containing the IF_8^- anion.[5,6] Since in a rigid molecule the space requirement of a sterically active free valence electron pair slightly exceeds that of a fluorine ligand,[7] one would predict that in IF_6^- there is enough space available for the free valence electron pair to be sterically active,[8] while in BrF_6^- there is little or no room left for a seventh ligand and, therefore, the free valence electron pair should be sterically inactive.

When the steric activity of the free valence electron pairs in AX_6E species is studied, two considerations should be kept in mind. First, the physical state of the AX_6E species is important.

In the solid state, crystal field effects can, depending on the symmetry of this field, induce either symmetry or distortion in a fluxional AX_6E species.[3] Therefore, these species should ideally be studied in the absence of crystal field effects, i.e. either as monomeric gaseous molecules or as dissolved ions. Second, for a fluxional compound the observed structure can appear to be different depending on the time scale of the technique used for the stucture determination. For example, the time scale for an X-ray crystal structure determination is very long. Although the time scale of the X-rays themselves is short, the signals are time averaged and, therefore, only a time averaged atom position can be seen, with the magnitude of the atomic thermal parameters serving as an indicator for the fluxionality of the species. The time scale of NMR spectroscopy is much shorter and approaches those of many fluxional rearrangements, thus frequently allowing their observation and the measurement of their energy barriers. Vibrational spectroscopy and electron diffraction provide the shortest time scale and are faster than the fluxional processes. They, therefore, result essentially in a picture of the fluxional species frozen in time.

Although Mossbauer spectra of solid $CsIF_6$ [8] and vibrational spectra of solid $CsIF_6$ and $CsBrF_6$ had previously been reported and were indicative of a distorted structure for the former[8,9] and a centrosymmetric D_{3d} structure for the latter,[10] no structural data were available on the free IF_6^- and BrF_6^- ions. During a recent study of $[N(CH_3)_4]^+$ salts of halogen fluorides,[11] it was found that $CsBrF_6$ and $CsIF_6$ have significant solubilities in CH_3CN. It, therefore, became possible to study the structures of the free BrF_6^- and IF_6^- ions in the absence of interfering crystal field effects.

The preparation of $CsBrF_6$ [10] and $CsIF_6$ [9] has previously been described. The compounds were handled in the dry N_2 atmosphere of a glove box. The CH_3CN (Baker, bioanalysed, having a water content of 40 ppm) was stored over P_2O_5, freshly distilled prior to its use, and handled either on a vacuum line or in the dry box. The final CH_3CN solvent that was used had a water content of less than 4 ppm.

Raman spectra of the CH_3CN solutions in flamed out glass NMR tubes were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer using the 488-nm exciting line of an Ar ion laser or the 647.1-nm line of a Kr ion laser, respectively. The ^{19}F NMR spectra were recorded on the same samples with a Varian Model EM 390 spectrometer equipped with a variable-temperature probe.

The BrF_6^- Anion. The Raman spectrum of a saturated CH_3CN solution of $CsBrF_6$ is shown in Figure 1. Three Raman active bands are observed at 565, 450 and 240 cm^{-1}, in excellent

agreement with the values of 562, 451 and 243 cm^{-1} previously reported[10] for the solid. Of these, the 565-cm^{-1} band is highly polarized, whereas the 450- and the weak 240-cm^{-1} lines are depolarized. The observed number of bands, their relative intensities and polarization ratios are in excellent agreement with expectations for the octahedral point group O_h.

In the solid state, the space group of $CsBrF_6$ had been reported to be either $R3m(D^5_{3d})$ or $R3(C^2_{3i})$, thus resulting for BrF_6^- in D_{3d} symmetry.[10] Although the Raman spectrum of BrF_6^- should not differ by much on going from O_h to D_{3d} symmetry, we consider this alternative less likely than O_h for the following reasons:

(i) The relative intensities of the 550- and 450-cm^{-1} Raman bands are reversed in the solid phase compared to those in CH_3CN solution. This suggests the possibility of different point groups for BrF_6^- in the solid state and in solution.

(ii) A D_{3d} structure for the free BrF_6^- anion would require equal occupation of two opposite ligand sites by a single free valence electron pair. This could be accomplished by placing the free valence electron pair of BrF_6^-, for example, into a p-orbital (Structure I). From a large body of experimental data it is known, however, that a free valence electron pair occupies only one coordination site at a time. Thus, in SF_4 the free valence electron pair occupies only one equatorial site (Structure II) and not two axial sites (Structure III)

(I)   (II)   (III)
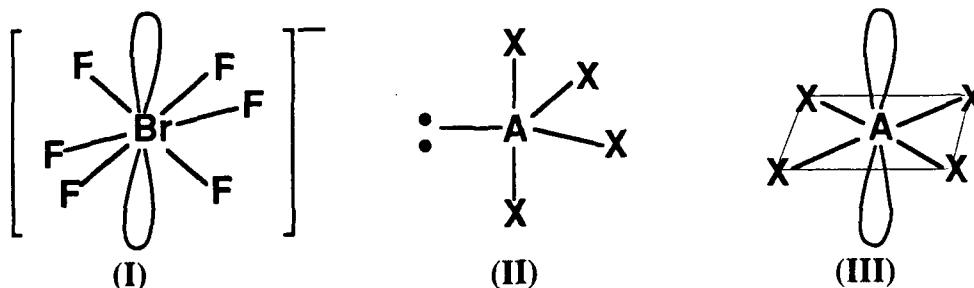
despite the fact that pseudo-octahedral strucures tend to be energetically more stable than pseudo-trigonal bipyramidal ones. The possible assignment for D_{3d} symmetry to BrF_6^- in solid $CsBrF_6$ [10] does not conflict with this conclusion. The D_{3d} symmetry could either reflect the site symmetry of BrF_6^- in the crystal or be the result of a slight compression of the BrF_6^- octahedra due to crystal packing effects.

Since the above Raman spectrum suggests that on the time scale of vibrational spectroscopy the BrF_6^- anion is octahedral, the question remained whether the octahedron is rigid or fluxional. ^{19}F NMR spectroscopy was used to answer this question. For a nonfluxional BrF_6^- octahedron, Br-F spin-spin coupling should be observable as, for example, in BrF_6^+ which exhibits a Br-F coupling constant of about 1580 Hz,[4] because the bromine central atom would be located in an electrically symmetric field and quadrupole relaxation would be minimal. The ^{19}F NMR spectrum of BrF_6^- in CH_3CN, however, consisted over the temperature range -60° to +40° C of a single resonance at $\emptyset = 94$ with an almost temperature independent line width of about 80 Hz with no detectable spin-spin coupling. This rules out the possibility of a rigid octahedral structure for BrF_6^-. The possibility of explaining the absence of Br-F spin-spin coupling in BrF_6^- by the presence of maybe a trace of free BrF_5 and an ensuing rapid exchange was also ruled out. It was shown that the addition of 20% of CsF, which would complex any free BrF_5 as BrF_6^-, to the sample did not alter the BrF_6^- signal.[12] It can, therefore, be concluded that the free BrF_6^- anion is octahedral on a vibrational spectroscopy time scale, but fluxional on the slower NMR time scale.

The question might be raised whether a small distortion of BrF_6^- from O_h should be observable in the Raman spectrum. Although we did not calculate theoretical Raman spectra for BrF_6^- as a function of varying degrees of distortion from O_h, the Raman spectra of gaseous XeF_6[13] and the free IF_6^- anion (this work) strongly deviate from the predictions for O_h. It, therefore, appears safe to conclude that in free BrF_6^- the distortion from O_h, if any at all, must be rather small.

The IF_6^- Anion. The Raman spectrum of a saturated solution of $CsIF_6$ in CH_3CN is shown in Figure 2. Due to the lower solubility of $CsIF_6$ in CH_3CN, the spectrum is of lower intensity and quality than that of $CsBrF_6$. However, based on the complexity of the observed spectrum, i.e. at least three polarized Raman bands with a possible splitting of the highest frequency vibration due to Fermi resonance, it appears safe to conclude that free IF_6^- is not octahedral and does not have the same structure as BrF_6^-.

The ^{19}F NMR spectrum of IF_6^- in CH_3CN consisted of a singlet at $\emptyset = 13$ with a line width of about 40 Hz at -40°C which broadened slightly with increasing temperature possibly due to a quadrupolar effect. The absence of observable I-F spin-spin coupling[14] rules out the possibility of a rigid octahedron, and the observation of a single sharp signal augurs also against a rigid distorted structure containing several nonequivalent fluorine atoms. Hence, it can be concluded that free IF_6^- is distorted on the time scale of vibrational spectroscopy and fluxional on the slower NMR time scale.

In conclusion, the Raman data suggest that on the fast time scale of vibrational spectroscopy the free BrF_6^- anion is octahedral while on the slower NMR time scale it is fluxional. Contrary to BrF_6^-, the free IF_6^- anion is strongly distorted on the vibrational spectroscopy time scale and again fluxional on the slower NMR time scale. These results demonstrate that in BrF_6^- the bromine free valence electron pair is sterically inactive, while in IF_6^- the iodine free valence electron pair is sterically active. This difference is attributed to the smaller size of the bromine central atom, which with its maximum coordination number of six toward fluorine cannot accommodate a seventh ligand. The observation of fluxionality for both BrF_6^- and IF_6^- is not surprising in view of the fact that the ease of delocalization of the free valence electron pair can provide a low energy path for the deformation of these ions.

The failures to prepare a stable ClF_6^- anion[15] are not attributed to steric effects since the maximum coordination number of chlorine toward fluorine is the same as for bromine, i.e. six, as shown by the existence of the ClF_6^+ cation[16,17] and the fact that ClF_5 undergoes rapid exchange with either CsF [18] or FNO [19] in ^{18}F radiotracer experiments. This conclusion is obviously based on the assumption that by analogy with BrF_6^- the chlorine free valence electron pair in ClF_6^- can be accommodated in a sterically inactive, centrosymmetric orbital. In our opinion, the instability of ClF_6^- is most likely due to the expected decrease in Lewis acidity in the series $IF_5 > BrF_5 > ClF_5$. By analogy to BrF_6^-, the free ClF_6^- anion should also be octahedral, contrary to previous predictions of C_{3v} symmetry made on the basis of the VSEPR rules[1,2] and the Laplacian of the calculated electronic charge distribution.[20]

Finally, we would like to emphasize the need for fast time scale methods when searching for the actual structures of fluxional molecules, while the slower methods can yield valuable information on the dynamics of the intramolecular motions. For ions it is desirable to study, whenever possible, the free ions and not the solids in order to avoid crystal field effects, which can impose either order or disorder on fluxional ions.[3]

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DIAGRAM CAPTIONS

Figure 1. Raman polarization spectra of $CsBrF_6$ in CH_3CN solution. The weak band marked by an asterisk is due to BrF_4^-, and the band marked by a diamond belongs to CH_3CN.

Figure 2. Raman polarization spectra of $CsIF_6$ in CH_3CN solution. The band marked by a diamond is due to CH_3CN.